THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

KRAFT LIQUOR CORROSIVITY - DETERMINATION OF SULFUR COMPOUNDS

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SUMMARY

At the First IPC Corrosion Forum held at The Institute of Paper Chemistry (June, 1979), the proper characterization of sulfide, thiosulfate, sulfite, and polysulfide in kraft liquors was considered.

As a result of these discussions, it became clear that liquor characterization has two major drawbacks: the current analytical techniques in use and the stability of the sulfur species. Accordingly, a research plan was proposed that consisted of two phases.

Phase I was a review of current mill methods and techniques and their principles. Phase II evaluated available analytical techniques, including a study of the effect of liquor age and storage (sampling) procedure on the stability of sulfur species in white and weak black liquors.

The analytical methods currently in use for sulfide analysis in white liquor are titration (TAPPI T624 os-68), ABC titration, potentiometric titration, and differential pulse polarography (DPP). A comparison of these methods and techniques was conducted for ten white liquors. Results indicated that all methods and techniques are reliable except the ABC indicator method.

The TAPPI and DPP methods for sulfite and thiosulfate analysis in white liquor were compared. Based on recovery tests on standard solutions, we have concluded that the TAPPI method is reliable for thiosulfate analysis but not for sulfite determination in white liquor. DPP was found to be a reliable technique for thiosulfate and sulfite analyses when the standard curve method is used instead of

the standard addition method. Although DPP is less time-consuming than the TAPPI method, the latter places much less demand on analytical equipment.

Polysulfide sulfur analysis in white liquor was investigated using TAPPI T624 os-68, DPP, the Mead Amalgam method, and UV spectrophotometry. Based on recovery tests in standard solutions and in real liquors, the Mead Amalgam and UV spectrophotometric methods are very reliable. The UV method is the most time efficient and reproducible of all methods. DPP is not recommended for polysulfide sulfur analysis.

Sulfide analysis in black liquor was determined by TAPPI T 625 ts-64, the ABC pH method, automatic potentiometric titration, and DPP. Based on recovery tests on real liquors, all methods were reliable except the ABC pH method. Potentiometric titration with $HgCl_2$ as titrant is the most time-efficient technique, and the TAPPI method is the most time-consuming technique.

The reliability of the TAPPI method and DPP for thiosulfate analysis in black liquor could not be established during this investigation. The use of the ion chromatographic method and the potentiometric titration technique with a sulfide ion selective electrode and $HgCl_2$ as titrant are recommended.

The stability of sulfide species in white and black liquors was investigated as a function of liquor age (2 weeks) and different storage conditions. Storage procedures using sulfide antioxidant buffers (SAOB I, II, III), air exclusion, and nitrogen blanket methods were investigated. SAOB I does not interfere with sulfide analysis in white liquors in contrast to SAOB II and III. For analytical determination of sulfide only, the use of SAOB I for white liquor storage is the recommended method. SAOB I cannot be used for corrosion studies, because it changes the chemical composition of the liquor. Therefore, the air exclusion and nitrogen

blanket methods are recommended. For black liquor studies, the air exclusi and nitrogen blanket storage procedures indicated that sulfide concentration re ined practically stable within the two-week storage time.

INTRODUCTION

At the First IPC Corrosion Forum, held in June, 1979, the reliability of the analytical methods currently available for the determination of sulfur species in kraft liquors was questioned. The reliability of the methods is important for correlations between the concentration of sulfur species and corrosion (1). The stability of sulfur compounds as a function of liquor age is also essential so that liquor chemistry in the corrosion lab is the same as in the mill. The sulfur species important to corrosion studies in liquor environments are sulfide, thiosulfate, sulfite, and polysulfide. A two-phase research program was implemented. Phase I was a review of the analytical methods currently in use by the paper industry. Phase II determined the reliability of existing methods and the effects of liquor age and storage time on sulfide stability in white and black liquors.

The analytical methods currently in use in the paper industry are shown in Table I. The methods most widely used are TAPPI (2,3) and ABC methods (4). TAPPI Standard T 624 os-68 (2) is used for the determination of sulfide, thiosulfate, sulfite, and polysulfide sulfur in white and green liquors. The principle of the method is based on iodimetric titration. This is a direct method in which substances such as sulfide, thiosulfate, and sulfite having an oxidation potential lower than the iodine-iodide ($I_2 + 2e \rightleftarrows 2I^-$) system are oxidized by iodine. The TAPPI procedure is labeled as being time-consuming, requiring numerous steps for the analysis of each of the sulfur species. The multitude of steps is a result of the nonselective nature of iodine in oxidizing sulfide, thiosulfate, and sulfite. However, this method was found reliable for the determination of sulfide and thiosulfate. It was unreliable for the determination of sulfite in white liquors.

TABLE I Here

TABLE I

METHODS AND TECHNIQUES FOR SULFIDE, THIOSULFATE, SULFITE, AND POLYSULFIDE SULFUR ANALYSIS

Liquor	Method	Technique	Equipment	Sulfur Species Tested
White	ABC (indicator)	Manual	Analytical glassware[a]	Sulfide
White/ Black	ABC (pH)	Automatic	Mettler DL40 MemoTitrator Mettler GA 40 Printer	Sulfide
White	TAPPI T 624 os-68	Manual	Analytical glassware[a]	Sulfide, thiosulfate, sulfite, and polysulfide sulfur
Black	TAPPI T 625 ts-64	Manual	Analytical glassware[a]	Sulfide, thiosulfate, and sulfite
White	• Potentiometric titration by • $AgNO_3$ $HgCl_2$	Manual Automatic	pH meter, analytical glassware Mettler DL40 MemoTitrator Mettler GA 40 Printer	Sulfide
White/ Black	• Potentiometric titration • Sulfide electrode $AgNO_3/HgCl_2$	Automatic	Metrohm E636 Titroprocessor E649 Magnetic stirrer E635 Titrating stand	Sulfide
White	• Potentiometric titration	Automatic	Metrohm E636 Titroprocessor E649 Magnetic stirrer	

Another widely used analytical method in the paper industry is the ABC acid-base titration method (4). The ABC method consists of three distinct and continuous titration steps; each is a measure of the following:

A step: Effective alkali = $NaOH + 1/2\ Na_2S$

B step: Active alkali = $NaOH + Na_2S$

C step: Total alkali = $NaOH + Na_2S + Na_2SO_3$

By simple mathematical manipulations (4), the A, B, and C results can be used to calculate the concentrations of NaOH, Na_2S, and Na_2CO_3. The end point in the A, B, and C acid-base titration steps can be determined either colorimetrically by the use of indicators (phenolphthalein and methyl orange) or potentiometrically by the use of a pH-meter (where the end point is identified when the desired pH is reached). The colorimetric method and the potentiometric method will be referred to in this report as the indicator and pH methods, respectively. In our study, we were interested only in the determination of Na_2S.

Based on the pH-method, the ABC titration can be partially or fully automated by the use of automatic analyzers in conjunction with automatic turntables. Some paper companies are using fully automated units. This automation has achieved the following: freeing the analyst (operator) for other duties while the analysis is being performed, shorter analysis time, and less possibility of human error (during analysis and calculation).

Despite the simplicity and successful use of the ABC method (especially the pH method) in white and green liquors, there are some problems encountered with black liquor analysis. The presence of organic phenols in the black liquors seems to impart a buffering action to the liquor, leading to erroneous results. The use of the ABC pH method for the determination of Na_2S in black liquor will be discussed later in this report.

The effect of liquor age, sampling, and storage on the stability of the sulfide species has also been studied. The following storage conditions were evaluated:

- Minimizing air entrainment by filling the liquor sample bottle to the top and capping immediately
- Nitrogen purged on top of the liquor
- Addition of sulfide antioxidant buffers (SAOB)

Simulating liquor transport from the mill to a laboratory, a liquor age of two weeks was studied. The results and implications are described in the following sections.

This report describes an investigation of methods and techniques for sulfur analyses in kraft liquors and the stability of sulfide species as a function of liquor age. It also serves as a manual for all the methods and techniques studied. As such, this report will be of value to analysts who lack sufficient familiarity in analytical chemistry.

PHASE I RESULTS - A REVIEW

Potentiometric methods are reported for the determination of Na_2S sing a sulfide ion selective electrode. Three types of methods are identified: the direct potentiometric method, the incremental method, and potentiometric titration. The direct method involves the measurement of the electrode potential (vs. a reference electrode), which is related to the activity or concentration of the tested species. In the incremental method, the concentration of the tested species is calculated from the change in potential difference before and after the addition of a known increment of the liquor to the known reagent or vice versa. Potentiometric titration is based on the measurements of the electrode potential (vs. a reference electrode) while a titrant of known concentration is increasingly added to the tested solution. Potentiometric titrations generally offer an increase in accuracy and precision at the cost of increased time. The accuracy is increased because measured potential differences are used to detect rapid changes in activity (concentration) that occur at the equivalence point (end point) of the titration. Thus, it is the change in potential vs. titrant volume and not the absolute value of the potential which is of interest in potentiometric titration. The rate of potential change in potentiometric titration is usually greater than the response slope, which limits precision in direct potentiometry.

As mentioned by Noel (5), potentiometric methods were reported as early as 1946 (6). In situ direct potentiometric measurements were approached by Cooper (7), who proposed the use of a silver sulfide-coated silver billet electrode directly in weak black liquor to continuously monitor the sulfide in the liquors. The author emphasized that problems with the electrode response may be encountered for varying liquor pH and temperature values.

The incremental technique for the determination of sulfide in liquor using a cadmium ion selective electrode has been reported by Frant and Ross (8). Although the cadmium ion incremental technique has been shown to be inadequate for sulfide analysis in black liquor (9), the ion-selective electrode procedures remained useful (10).

The use of potentiometric titration for the analysis of sodium sulfide is discussed in numerous publications (11-16,7). In 1973, Fisher (10) developed the sulfide ion selective electrode for potentiometric titration in sulfide determination, using mercuric chloride as the titrant. Another titrant commonly used is silver nitrate ($AgNO_3$). Because of errors due to frequent clogging of the sulfide ion selective electrode during titration of black liquor with Ag_2S, the titration with $HgCl_2$ has become more attractive (14). Bilberg (17,18) also found that the mercuric chloride method is superior, especially for liquors containing organic materials and polysulfides. In our investigation, we have also found that the silver nitrate method is more time-consuming than the mercuric chloride method, probably due to an interaction between the organic and silver nitrate and/or due to the clogging of the electrode as indicated by Danielsen et al. (14).

Another titrant used for potentiometric determination of sodium sulfide is cadmium nitrate. This titrant is suitable with sulfide antioxidant buffers (SAOB), because $HgCl_2$ reacts with ascorbic acid, which is an ingredient of these buffers (5,8,19). Sulfide antioxidant buffers are used to eliminate or reduce the air oxidation of sulfide in liquor environments.

Potentiometric titration can be performed either manually or automatically. In addition to their use for sulfide determination, potentiometric titrations are used for sulfite and thiosulfate analysis (3,11,13,20-21). The TAPPI T 625 ts-64

(3) is the most widely known and applied. However, the TAPPI method is time consuming and the reliability is not well established; the paper industry is still searching for other techniques for sulfite and thiosulfate analysis.

Polarography, like potentiometry, is an electrochemical technique which appears attractive and challenging. Polarography, developed by Heyvorsky (22) in 1922, is the study of current-potential curves obtained at a microelectrode (dropping mercury electrode) when the rate of the electrochemical reaction of the tested species is controlled by diffusion. Renard (23) and Canterford (24) have decribed the use of ac polarography (25) for the analysis of sulfur compounds in pulping liquors. The differential pulse polarographic (DPP) technique (25) is most commonly used in the paper industry. Its use has been reported by Noel (5), Canterford (26), and Youssefi and Birke (27). Noel (5) emphasized that the differential pulse technique is fast, because sample preparation is minimized relatively free of interference. The analytical lab of Nekoosa Edwards (19) has found the DPP technique reliable for the determination of sulfide in black liquor before and after oxidation.

Besides the TAPPI, ABC, potentiometric, and polarographic techniques, there are other methods reported in the literature for analysis of sulfur compounds. These are ion chromatographic (28) and absorptiometric (29) (spectrophotometric) methods. Ion chromatography, developed by Dow Chemical Co., is a relatively new technique. Small et al. (18) published the first paper in 1975 describing the use of the ion chromatograph. According to Franklin (30), the ion chromatography process consists essentially of three steps: ion separation, eluant suppression, and conductivity detection of ions. The technique is fast (sulfate, thiosulfate, sulfite, sulfide, and oxalate can be determined in 30 minutes) (30) and versatile (sodium, potassium, ammonium, aluminum, magnesium, phosphate, chloride, carbonate, and organic acids can

also be determined). The state of the art of ion chromatography is reviewed by Pohl and Johnson (31). Although this technique was not available at the time of this investigation, it is strongly recommended for sulfur compound analysis.

Polysulfide determination in liquor environments is extremely important from the corrosion standpoint. The analytical methods available are the TAPPI, Mead amalgam, UV spectrophotometric, and DPP techniques. The only direct method is UV spectrophotometry; i.e., it senses the species directly. In the other methods, polysulfide must be transformed into another species. In the TAPPI and DPP methods, polysulfide is transformed to sodium thiosulfate ($Na_2S_2O_3$) and sodium sulfide (Na_2S) via the following reaction:

$$\underset{\text{Sodium polysulfide}}{Na_2S_x} + (x-1)\ Na_2SO_3 \rightleftarrows (x-1)\ Na_2S_2O_3 + Na_2S$$

Polysulfide sulfur can be calculated by determining thiosulfate before and after addition of sodium sulfite.

In the Mead process, polysulfide is reduced by sodium amalgam to sulfide by the following reaction (3):

$$Na_2S_x + \underset{\text{sodium amalgam}}{(2x-2)\ NaHg_n} \rightarrow X\ Na_2S + (2x-2)\ Hg_n$$

Polysulfide sulfur is calculated by determining the concentration of sodium sulfide before and after reduction.

PHASE II - SULFUR ANALYSES IN KRAFT LIQUORS

ANALYSIS OF SULFIDE, THIOSULFATE AND SULFITE IN WHITE LIQUOR

The methods investigated here for sulfide analysis are TAPPI Standard T 624 os-68, ABC titration, manual and automatic potentiometric titration, and the DPP method. ABC titration was studied by the indicator and pH methods. In manual potentiometric titration, mercuric chloride and $AgNO_3$ are used as the titrants. Automatic potentiometric titration was conducted by two different instruments, a Metrohm E636 Titroprocessor and a Mettler DL40 MemoTitrator. The analyses of thiosulfate and sulfite were conducted by the TAPPI Standard T 624 os-68 and DPP methods. The principles of all the methods and techniques used for sulfide, thiosulfate, and sulfite analysis are given in Appendix IV.

Comparison of Methods and Techniques for Sulfide, Thiosulfate, and Sulfite Analysis in White Liquor

Sulfide Analysis

Table II shows the comparisons among methods for sulfide analysis in 10 white liquors.

There is a satisfactory agreement between the results of the TAPPI, ABC automatic (pH-method), manual potentiometric titration using $HgCl_2$ and $AgNO_3$, automatic potentiometric titration by Mettler and Metrohm instruments, and the differential pulse polarographic (DPP) method. These methods are based on different principles (Appendix I) but gave very similar results. The standard deviation of sulfide determinations by each method showed that the reproducibility of the DPP method was not good throughout our investigation of all liquors. This could be due to the liquor, the technique or the instrument.

ABC manual titration consistently gave lower sulfide concentration than ABC automatic titration. The manual titration (indicator method) uses an indicator

(phenolphthalein) for the identification of the end point in the A and B steps. The automatic method determines the end point by reaching a preselected pH value. This method is conducted either manually with a pH meter or automatically with an automatic potentiometric titrator. In our comparison, the pH method was conducted automatically by a Mettler model DL40 MemoTitrator. The A step in the indicator method is terminated at pH = 8.3. The A step in the pH method is terminated at pH = 9.3. The latter pH is the pH at which the actual end point occurs for the titration of all NaOH and 1/2 Na_2S (4). Thus, more acid is needed in Step A of the indicator method compared with the pH method. Since the B step in both procedures is terminated at pH = 8.3 (i.e., the B result is equal in both methods), the sulfide concentration calculated from the A and B steps, equal to 2(B-A), is higher with the pH method than with the indicator method.

The data using the indicator method can be correlated with the data obtained by the pH method. The correlation curve is shown in Fig. 7. The results of the indicator method can also be improved by using thymolphthalein (4). The end point of the A step using thymolphthalein is reached at pH = 9.3 as in the ABC pH method (4).

The automatic potentiometric titration of Na_2S was conducted with two different instruments. The Metrohm E636 Titroprocessor often gave 2 or more end points, which left the operator to decide which end point was correct. Efforts were made to eliminate the spurious end points by varying the controlling parameters of the instrument. Modifying the measuring point density (ranging from few measuring points with large-volume steps to many measuring points with small-volume steps) and the kinetics (drift) proved to be unsuccessful, particularly for the weak black liquors.

Table II here

TABLE II

DIUM SULFIDE ANALYSIS BY DIFFERENT METHODS

Potentiometric Titration						
Automatic						
Mettler		Metrohm				Polarographic
				$Cd(NO_3)_2$		
$HgCl_2$	$AgNO_3$	$HgCl_2$	$AgNO_3$	Ag Elec.	Cd Elec.	DPP
30.5 ± 0.1	45.6 ± 0.1	30.4 ± 0.1	30.3 ± 0.2	30.1 ± 0.1	30.5 ± 0.1	29.0 ± 0.5
		29.2 ± 0.0	28.9 ± 0.1	29.4 ± 0.1	29.3 ± 0.2	31.0 ± 0.2
		25.8 ± 0.4	25.4 ± 0.1	25.7 ± 0.2	25.6 ± 0.1	26.8 ± 0.4
		32.6 ± 0.5	32.2 ± 0.1	32.1 ± 0.3	32.3 ± 0.1	32.2 ± 0.4
45.5 ± 0.6	45.6 ± 0.1	45.9 ± 0.1	45.7 ± 0.2	45.3 ± 0.1	45.3 ± 0.3	48.2 ± 0.0
36.3 ± 0.4	36.4 ± 0.0	36.2 ± 0.0	36.6 ± 0.1	36.3 ± 0.2	36.2 ± 0.2	36.9 ± 0.0
44.0 ± 0.3	44.4 ± 0.1	44.7 ± 0.2	44.6 ± 0.1	44.1 ± 0.2	44.0 ± 0.2	46.3 ± 0.7
46.8 ± 0.2	47.3 ± 0.1	47.2 ± 0.1	47.1 ± 0.1	46.5 ± 0.3	46.4 ± 0.4	49.6 ± 0.6
34.4 ± 0.1	34.6 ± 0.2	34.5 ± 0.1	34.6 ± 0.1	34.9 ± 0.1	34.1 ± 0.1	33.9 ±
45.3 ± 0.1	45.8 ± 0.1	45.7 ± 0.0	46.0 ± 0.3	45.7 ± 0.1	44.7 ± 0.7	48.0 ± 0.6
2 min 51 sec	5 min 18 sec	Approx. 20 min	Approx. 30 min	Approx. 30 min	Approx. 30 min	Approx. 20 min

time depends on how successful the sulfide removal step is.

The Mettler DL40 MemoTitrator always gave one end point and was significantly faster in end point determination. The rapid determination of a single end point is made possible through the flexibility of choice among five different titration principles and the control parameters. The most suitable titration principle and its optimum parameters can quickly and automatically be determined by a single performance of a "Learn Titration." The following example serves to illustrate this point. [In determining the best titration principle and its associated optimum control parameters for sulfide analysis with mercuric chloride, the operator first executes a "Learn Titration" using mercuric chloride as titrant. In less than one minute, the MemoTitrator completes the "Learn Titration" and selects "End Point Relative" as the best titration principle. The MemoTitrator also selects and lists the optimal control parameters, such as the end point potential region and the control band. Within the control band, the dispensing rate decreases as a function of the difference between the actual measurement value and the end-point value. When the difference is 0, the end point is reached and no more titrant is added. The control band is selected so that the control is optimally adapted to the change of the measured value in the end point range.]

There was a significant difference in speed between the Metrohm and Mettler methods. The Metrohm feeds a varying amount of titrant into the sample medium. Each volume must be processed according to the drift and kinetic parameters selected until the chosen parameters are met. The instrument then choses the next volume addition and processes the information until the drift parameters are again met. This sequence is continued until one or more end points is found. The Mettler continuously feeds and monitors potential change very rapidly until it approaches the end of the control band. It then slows down near the end-point potential and stops feeding reagent when the end-point potential is reached.

Change side label to - Na_2S Concentration (g/L) by ABC pH Method

Change bottom label to - Na_2S Concentration (g/L) by ABC Indicator Method

Figure 7. Correlation curve of Na_2S concentration determined by ABC indicator method and ABC pH method.

The reason the Metrohm often selects two or more end points is not fully understood. Perhaps it is due to the criteria used to differentiate end points, i.e., there may be more than one potential change near the true end-point region large enough to be classified as an end-point relative to the potential changes that occur outside the end point region.

The Mettler DL40 MemoTitrator is preferred for several reasons. First, the analysis time is significantly less. Second, the optimum titration principle and its associated optimal parameters can be determined rapidly and automatically using the "Learn Titration" function of the instrument. Conversely, selection of the optimal parameters using the Metrohm is often a combination of working knowledge of the instrument and a certain amount of trial and error. Third, the operation of the Mettler is easier to learn than the Metrohm. Finally, the Mettler is more advantageous in its consistent selection of only one end point.

An attractive feature of the Metrohm titrator is the automatic sample changing with subsequent automatic analyses. Also, an improved model of the Metrohm E636 titrator is now available; it has the added features of expanded memory (more data points) and an interface for a RS 242 (two-way) computer. In conclusion, the overall evaluation of each method and technique is listed below.

TAPPI Standard T 624 os-68.

Advantages:
- The method is reliable and does not require major equipment purchases.

Disadvantages:
- The method is very time consuming - about 45 minutes. More than 45 minutes is spent if the sulfide removal step is not successfully and properly done from one attempt.

- Because of the multitude of steps needed for the sulfide analysis, there is usually a chance of human error.
- The method requires periodic standardization of the key reagents - sodium thiosulfate and iodine.

ABC indicator method (manual)

Advantages:

- The analysis time is very short.
- The method can be reliable if 1) thymolphthalein is used in Step A instead of phenolphthalein and 2) a calibration curve is established between the indicator and pH method.
- No major equipment is necessary to run the manual technique.
- If Acculute Solutions* of NaOH and HCl are used, the preparation time for analysis can be reduced tremendously.

Disadvantages:

- Human error is possible in detecting the end points.
- Glassware cleaning is tedious and time consuming.
- Titration must be performed under a ventilation hood.

ABC pH method (automatic)

- The method is reliable and fast.
- The automation of the technique frees the analyst or operator for other duties.

Disadvantages:

- Expensive equipment is needed
- The analysis must be performed under the ventilation hood.

Manual Potentiometric Titration - $HgCl_2$

Advantages:

- The method is very reliable and fast.
- The titrant $HgCl_2$ is a primary standard, so no standardization is needed as in the case of $Cd(NO_3)_2$.

*Prepackaged concentrated solutions which can be diluted and considered as standards.

- For the manual technique, no major equipment purchases are needed.

Disadvantages:
- The method necessitates continuous recording of potential and increments of titrant added.

Automatic Potentiometric Titration - Mettler - $HgCl_2$

Advantages:
- The method is very reliable and has the shortest analysis time of all methods.
- The automation of the titration frees the operator for other duties.

Disadvantages:
- The Mettler instrument is expensive.

Automatic Potentiometric Titration - Mettler - $AgNO_3$

Advantages:
- The method is very reliable and has the second shortest analysis time of all methods.
- The automation of the titration frees the operator for other duties.

Disadvantages:
- Expensive.

Automatic Potentiometric Titration - Metrohm - $HgCl_2$ and $AgNO_3$

Advantages:
- The method is reliable and reasonably fast.
- Since the procedure, plotting the curve, and calculating the data are run automatically, the analyst is freed to perform other jobs.
- The two titrants can be prepared as primary standards, i.e., no standardization is required.

Disadvantages:
- The possibility arises for the appearance of multiple end points, i.e., some guessing as to the correct end point is expected.

- Expensive.
- No advantage in time saving compared with the manual technique.

Automatic Potentiometric Titration - Metrohm-$Cd(NO_3)_2$

Advantages:
- The method is reliable and reasonably fast.
- Since the procedure, plotting the curve, and calculating the data are automatic, the analyst is freed for other jobs.
- The use of this titrant is very suitable when sulfide autoxidant buffer is added to the liquor.

Disadvantages:
- Standardization of $Cd(NO_3)_2$ is necessary, so additional preparation time is required.
- The possibility for multiple end points is greater than in the case of $HgCl_2$ and $AgNO_3$.
- The shape of the potential vs. titrant curve is poor.
- A characteristic of the $Cd(NO_3)_2$ titration is the slow potential drift.

Automatic Potentiometric Titration - Metrohm Cd-electrode - $Cd(NO_3)_2$

Advantages:
- The method is reliable and reasonably fast.
- Since the procedure, plotting the curve, and calculating the data are automatic, the analyst is freed for other jobs.
- The use of this titrant is quite suitable when sulfide autoxidant buffer is added to the liquor.

Differential Pulse Polarography (DPP)

Advantages:
- The method generally is reliable.
- The time of analysis is moderate.

- Since the method is automatic, it frees the analyst for other duties.

Disadvantages:

- The method does not exhibit good reproducibility.
- Preparation of sulfide standard is necessary. For this preparation a ventilation hood is needed.
- Standardization of the standard has to be done periodically, which is a time-consuming process.
- Sample preparation is required.

Sodium Thiosulfate and Sodium Sulfite Analysis

The available techniques for thiosulfate and sulfite analysis are the TAPPI and Differential Pulse Polarographic DPP methods. The comparison of analyses for ten white liquors is shown in Table III. There was not good agreement between methods for thiosulfate and sulfite analyses.

The reliability of the TAPPI procedure for thiosulfate and sulfite analyses was investigated. Standard solutions were prepared by the addition of sodium sulfite and sodium thiosulfate to a base solution containing 5 g/L sodium hydroxide (NaOH). All steps of TAPPI T 624 os-68 were conducted to determine sulfite and thiosulfate in the standard solution. The results (Table IV) indicate that the TAPPI procedure is not reliable for sulfite analysis. This can be attributed to the following: (1) decomposition of sulfite during the testing period, about 1/2-hour (e.g., air exposure may lead to the oxidation of sulfite to sulfate); (2) possible interaction between sulfite and zinc carbonate, which is added for sulfide removal; 3) $\pm$ 4 milliequivalent/liter error allowed by the TAPPI procedure. Each factor was evaluated.

TABLE III here

TABLE III

WHITE LIQUOR SODIUM THIOSULFATE ANALYSIS BY DIFFERENT METHODS

	WL-1	WL-2	WL-3	WL-4	WL-5	WL-6	WL-7	WL-8	WL-9	WL-10
Tappi	4.3 ± 0.1	5.8 ± 0.1	7.2 ± 0.1	5.0 ± 0.1	6.4 ± 0.1	4.1 ± 0.1	3.8 ± 0.1	3.8 ± 0.1	4.8 ± 0.1	4.4 ± 0.1
DPP	5.6 ± 0.1	7.3 ± 0.2	8.0 ± 0.3	5.7 ± 0.1	4.7 ± 0.1	4.4 ± 0.2	3.4 ± 0.2	4.7 ± 0.3	6.4 ± 0.3	5.4 ± 0.3

WHITE LIQUOR SODIUM SULFITE ANALYSIS BY DIFFERENT METHODS

	WL-1	WL-2	WL-3	WL-4	WL-5	WL-6	WL-7	WL-8	WL-9	WL-10
Tappi	1.1 ± 0.2	0.7 ± 0.1	0.8 ± 0.1	1.7 ± 0.1	0.6 ± 0.1	1.6 ± 0.1	0.5 ± 0.3	0.8 ± 0.1	1.7 ± 0.1	0.9 ± 0.1
DPP	0.6 ± 0.1	0.3 ± 0.0	0.6 ± 0.1	1.0 ± 0.1	0.3 ± 0.1	1.3 ± 0.1	0.08 ± 0.02	0.3 ± 0.0	0.9 ± 0.1	0.3 ± 0.1

TABLE IV

ANALYSIS OF STANDARD SOLUTIONS CONTAINING VARIOUS AMOUNTS OF Na_2SO_3 AND $Na_2S_2O_3$

Standard solution, nominal concentration (g/L)		Analysis of standard solution, actual concentration (g/L)	
Na_2SO_3	$Na_2S_2O_3$	Na_2SO_3	$Na_2S_2O_3$
0.0	5.0	0.1 $\pm$ 0.0	4.9 $\pm$ 0.1
1.7	5.0	0.6 $\pm$ 0.2	4.9 $\pm$ 0.1

A 5 g/L sodium sulfite solution was prepared in acidic (0.5M acetate buffer), neutral (water), and basic (5 g/L NaOH) media. Direct iodine titration (iodimetric method) was used to determine the Na_2SO_3 present. The analyses were performed immediately after solution preparation (0 hour) and half an hour later. The results (Table V) indicate that there was no discernible decomposition of sodium sulfite over the 1/2-hour testing period.

Next, a standard solution containing 0.9 g/L Na_2SO_3 and 4.0 g/L $Na_2S_2O_3$ was prepared. Sulfite and thiosulfate analyses were performed by steps 2 ("S.F.R.C.$_b$") and 3 ("S.F.R.C.$_c$") of the TAPPI procedure, using various amounts of $ZnCO_3$. The results (Table VI) show that $ZnCO_3$ drastically decreases the concentration of Na_2SO_3 but has no effect on $Na_2S_2O_3$. The decrease in Na_2SO_3 may be attributed to the formation of zinc sulfite ($ZnSO_3$) or a complex composed of zinc and sulfite. This indicates that if excess $ZnCO_3$ is used to remove sulfide according to the TAPPI procedure, large errors are expected in sulfite analysis.

A thought experiment was conducted to investigate the effect of allowing a $\pm$ 4 milliequivalents/liter error. First, the $\pm$ 4 milli equivalent/L error was allowed in the "S.F.R.C.$_b$" step, whereas it was assumed that "S.F.R.C.$_c$" was kept at a constant

value (i.e., no errors allowed). Second, an error of ± 6 milliequivalents liter was allowed for "S.F.R.C.$_c$," whereas "S.F.R.C.$_b$" was kept at a constant value. The results (Table VII) indicate that the error allowed by the TAPPI standard may result in a change of ± 0.1 g/L for $Na_2S_2O_3$ and ± 0.3 g/L for Na_2SO_3 when "S.F.R.C.$_b$" is changed and "S.F.R.C.$_c$" is kept constant. When a titrator error of ± 6 milliequivalents/L is allowed for "S.F.R.C.$_c$" while "S.F.R.C.$_b$" is kept constant, an error of ± 0.2 g/L for $Na_2S_2O_3$ and ± 0.1 g/L for Na_2SO_3 is anticipated. A small error in "S.F.R.C.$_b$" may contribute to about 100% error and more, when the concentration of Na_2SO_3 in the liquor is as low as 0.3 g/L (see Table VII). Based on the concentration levels of Na_2SO_3 and $Na_2S_2O_3$ in white liquors (see Table III), it is concluded that the error allowed by the TAPPI standard significantly affects only sodium sulfite analysis. The interference by $ZnCO_3$ and the allowable titration error render the TAPPI procedure unreliable for sulfite determination.

TABLE V

DECOMPOSITION STUDY OF 5 g/L Na_2SO_3 SOLUTION

Time of Testing hours	Analysis of Na_2SO_3, g/L in Various Media		
	0.05M Acetate Buffer (acidic medium)	H_2O (neutral medium)	5 g/L NaOH basic medium
0	4.93	4.95	4.90
1/2	4.96	4.92	4.90

The disadvantages of the TAPPI standard are (1) the time consumed in the experiment (1 1/4 hour for thiosulfate and sulfite), (2) the requirement for operator attention throughout the analysis, (3) the multitude of steps that may result in frequent errors. An automatic titroprocessor eliminates these disadvantages.

The DPP technique was also investigated for the analysis of $Na_2S_2O_3$ and Na_2SO_3. The investigation was conducted with regard to the following: (1) proper

concentration of the buffer acetate medium, (2) the standard addition vs. standard curve method, and (3) the possibility of interaction between Na_2S and Na_2SO_3.

TABLE VI

EFFECT OF $ZnCO_3$ ON SULFITE AND THIOSULFATE ANALYSIS IN A STANDARD SOLUTION CONTAINING 0.9 g/L Na_2SO_3 and 4.6 g/L $Na_2S_2O_3$

$ZnCO_3$, mL	Na_2SO_3, g/L	$Na_2S_2O_3$, g/L
0	0.86	4.61
1	0.56	4.71
10	0.34	4.65
30	0.19	4.55
60	0.08	4.71

Two concentrations of the acetate buffer were tested (0.025M and 0.5M). The 0.5M concentration was proposed and used by Renard (23), whereas 0.025M was used by L. Noel (5). Two standard solutions were prepared containing 7.66 g/L and 0.766 g/L $Na_2S_2O_3$. Using the standard addition method, better results were obtained with the 0.025M buffer at the high concentration level (7.66 g/L). At the low concentration range, the 0.5M buffer was a better medium for $Na_2S_2O_3$ analysis. Two Na_2SO_3 concentrations were tested (2.255 g/L and 0.564 g/L). The two buffer concentrations gave high values at 2.255 g/L, with errors ranging between 30 and 40%. At 0.564 g/L, the error involved was between 15 and 22% at a low concentration of buffer and 32 and 34% at a high concentration of buffer. Significant errors at both buffer concentrations exist using the standard addition method.

In the standard addition vs. standard curve methods, the analysis of known concentration of Na_2SO_3 in 0.5M acetate buffer was conducted by the following three calculation methods: (1) Method 1 consists of sample analysis against standards

using standard addition; (2) Method 2 consists of sample analysis against a 1-point standard using the standard curve; (3) Method 3 consists of sample analysis against a three-point standard using the standard curve.

TABLE VII

THE EFFECT OF ALLOWING ± 4 MILLIEQUIVALENT/L ERROR IN "S.F.R.C.$_b$" AND ± 6 MILLIEQUIVALENT/L ERROR IN "S.F.R.C.$_c$" IN Na_2SO_3 AND $Na_2S_2O_3$ ANALYSIS

"S.F.R.C.$_b$," eg/L	Volume of $Na_2S_2O_3$ used for "S.F.R.C.$_b$," mL	"S.F.R.C.$_c$," eg/L	$Na_2S_2O_3$, g/L	Na_2SO_3, g/L
0.0594	27.03	0.277	4.9	1.8
0.0554	27.23	0.277	5.0	1.5
0.0514	27.43	0.277	5.1	1.2
0.0404	27.98	0.258	4.9	0.6
0.0364	28.18	0.258	5.0	0.3
0.0324	28.38	0.258	5.1	0.0
0.0721	26.40	0.378	6.9	1.8
0.0681	26.60	0.378	7.0	1.5
0.0641	26.80	0.378	7.1	1.2
0.0530	27.35	0.359	6.9	0.6
0.0490	27.55	0.359	7.0	0.3
0.0450	27.75	0.359	7.1	0.0
	Volume of I_2 used for "S.F.R.C.$_c$," mL			
0.0554	6.775	0.271	4.9	1.6
0.0554	6.925	0.277	5.0	1.5
0.0554	7.075	0.283	5.1	1.4
0.0364	6.300	0.252	4.9	0.4
0.0364	6.450	0.258	5.0	0.3
0.0364	6.600	0.264	5.1	0.2
0.0681	9.300	0.372	6.9	1.6
0.0681	9.450	0.378	7.0	1.5
0.0681	9.600	0.384	7.1	1.4
0.0490	8.825	0.353	6.9	0.4
0.0490	8.975	0.359	7.0	0.3
0.0490	9.125	0.365	7.1	0.2

Method 1 consists of standard addition or spiking the liquor with a known concentration. The analysis was conducted on one sample containing 2.038 g/L Na_2SO_3, and the spiking was done with three different solutions containing 2.038, 4.076, and 6.114 g/L Na_2SO_3. The results (Table VIII) revealed more error is encountered the higher the concentration of spiking.

TABLE VIII

RESULTS OF METHOD 1 - STANDARD ADDITION

	Spike, concentration g/L		
Na_2SO_3 parameters	2.038	4.076	6.114
Peak potential, V	-0.596	-0.596	-0.596
Peak current, NA	1.104E2	1.119E2	1.077E2
Na_2SO_3 concentration, g/L	2.795	3.044	3.560
Error, %	37	49	75

Method 2 consists of the preparation of 1-point standard curves using 2.038, 4.076, 6.114, 8.152, and 10.190 g/L Na_2SO_3 standards. (Each curve is constructed from one standard solution.) Using the five standard curves, the concentration of Na_2SO_3 in a standard solution containing 2.038 g/L Na_2SO_3 is determined. The results shown in Table IX indicated that the 1-point standard method works well when the sample concentration is very close to the standard concentration of the 1-point standard curve.

Method 3 consists of the preparation of a 3-point standard curve using 3 standard solutions containing 2.038, 4.076, and 6.114 g/L Na_2SO_3. This curve is then used to determine the concentration of Na_2SO_3 in the standard solutions containing 2.038, 4.076, 6.114, and 10.190 g/L Na_2SO_3. The results shown in Table X indicated high accuracy. Based on the comparison of the various methods, it is

concluded that Method 3, the 3-point standard using the standard curve, is recommended for the determination of Na_2SO_3.

TABLE IX

RESULT OF METHOD 2 - 1-POINT STANDARD CURVE

	Standard Solution				
Na_2SO_3 parameters	2.038 g/L	4.076 g/L	6.114 g/L	8.152 g/L	10.190 g/L
Peak potential, V	-0.596	-0.596	-0.596	-0.596	-0.596
Peak current, NA	1.066E2	1.070E2	1.082E2	1.083E2	1.087E2
Na_2SO_3 concentration, g/L	2.063	2.310	2.646	2.784	2.843
Error, %	1	14	30	37	39

TABLE X

RESULTS OF METHOD 3 - 3-POINT STANDARD CURVE

	Standard Solution			
Na_2SO_3 parameters	2.038 g/L	4.0765 g/L	6.114 g/L	10.190 g/L
Peak potential, V	-0.596	-0.592	-0.592	-0.592
Peak current, NA	1.106E2	1.926E2	2.597E2	3.914E2
Na_2SO_3 concentration, g/L	2.082	4.101	6.011	10.43
Error, %	+2	+1	-2	+2

The analyses of $Na_2S_2O_3$ in liquors using the 3-point standard curve method was performed in the presence of 0.5M and 0.025M acetate buffers. The results (Table XI) indicate an agreement between the values determined by TAPPI and DPP using the 3-point standard curve method. Since TAPPI and DPP (by standard curve method) are reliable on standards, these methods are expected to be appropriate for liquor environments.

TABLE XI

ANALYSIS OF SODIUM THIOSULFATE BY THE TAPPI METHOD AND VARIOUS METHODS OF DIFFERENTIAL PULSE POLAROGRAPHY (DPP)

Liquors	WL-1 1	WL-2 2	WL-3 3	WL-4 4	WL-5 5	WL-6 6	WL-7 7	WL-8 8	WL-9 9	WL-10 10
\PPI	4.3 ± 0.1	5.8 ± 0.1	7.2 ± 0.1	5.0 ± 0.1	6.4 ± 0.1	4.1 ± 0.1	3.8 ± 0.1	3.8 ± 0.1	4.8 ± 0.1	4.4 ± 0
³P (3 point standard) 0.5M acetate buffer	4.9 ± 0.2	--	7.6 ± 0.5	--	6.5 ± 0.3	4.4 ± 0.1	--	--	5.9 ± 0.1	--
³P (3 point standard) 0.25M acetate buffer	4.8 ± 0.05		7.4 ± 0.06	--	6.9 ± 0.3	3.9 ± 0.08	--	--	5.7 ± 0.7	--
³P standard addition 0.5M acetate buffer	5.6 ± 0.1	7.3 ± 0.2	8.0 ± 0.3	5.7 ± 0.1	4.7 ± 0.1	4.4 ± 0.2	3.4 ± 0.2	4.7 ± 0.3	6.4 ± 0.3	5.4 ± 0

In the above study, the sulfite analysis by DPP was conducted on standard solutions containing Na_2SO_3 with or without $Na_2S_2O_3$. Since liquors also contain Na_2S, further study examined the effect of Na_2S on sodium sulfite analysis. Standard solutions were prepared by mixing Na_2S and Na_2SO_3. The results indicated that the higher the sulfide concentration, the lower the Na_2SO_3 concentration. When 30 g/L Na_2S was added to 2.4 g/L Na_2SO_3, the analysis of Na_2SO_3 revealed a 16.6% loss compared with the analysis in the absence of Na_2S. This could be related to possible interaction between Na_2S and Na_2SO_3.

The evaluation of each method follows.

TAPPI 624 os-68 - Thiosulfate

Advantages:

- The method is considered reliable based on our testing on standard solution.
- Only analytical glassware and a pH meter are needed.

Disadvantages:

- The method is very time-consuming; about 1 1/2 hours is counted as analysis time only.
- More time is required for analysis preparation, including standardization of iodine and sodium thiosulfate and preparation of the mercury pool for the "S.F.R.C.$_c$" step.
- The possibility of human error exists because of the multitude of steps needed.
- The method necessitates the continuous attention of the operator.

TAPPI 624 os-68 - Sulfite

Advantages:

- Less equipment demand than the DPP method, i.e., only simple glassware and pH meter are needed.

Disadvantages:
- The method is not reliable.
- The method is very time-consuming; about 1 1/2 hours is counted as analysis time only.
- More time is required for analysis preparation, including standardization of iodine and sodium thiosulfate and preparation of the mercury pool for the "S.F.R.C.$_c$" step.
- The possibility of human error exists because of the multitude of steps needed.
- The method necessitates the continuous attention of the operator.

Differential Pulse Polarograph DPP - Thiosulfate and Sulfite

Advantages:
- The method exhibits a relatively short analysis time of 20 minutes.
- Sulfite and thiosulfate analysis can be determined in one run.
- The method is considered reliable when a 3-point standard curve is used.

Disadvantages:
- Expensive.

POLYSULFIDE SULFUR ANALYSIS IN WHITE LIQUOR

The methods examined for polysulfide in white liquor were TAPPI T 624 os-68, DPP polarography, Mead amalgam, and UV spectrophotometry. In the TAPPI and DPP methods, the polysulfide sulfur is determined as follows: excess sulfite is added to the liquor to react with all polysulfide present to form thiosulfate and sulfide.

$$S_x^{2-} + (x-1)SO_3^{2-} \rightleftharpoons (x-1)S_2O_3^{1-} + S^{2-}$$

By determining thiosulfate concentration before and after the addition of sulfite, the concentration of polysulfide is determined. The TAPPI and DPP methods are referred to as indirect methods, because polysulfide is transformed to another species (thiosulfate) to which the methods are sensitive. The Mead amalgam method is also an indirect method, but the principle is different from that of the TAPPI and DPP methods. The only direct method is the UV spectrophotometric method (53). The principles and techniques required in each method are described in Appendix VI.

Comparison of Methods for Polysulfide Sulfur Analysis in White and Black Liquors

Polysulfide sulfur analysis was conducted in six kraft white liquors (WL-2 through 5, 7-8). A definite conclusion on the reliability of the technique could not be drawn from the results shown in Table XVII. Recovery tests were then conducted in real and simulated liquors to investigate the reliability of the techniques. The simulated liquors containing 1 and 3 g/L polysulfide sulfur were prepared by the following procedure:

Preparation of 160 g/L NaOH and 31.2 g/L Na_2S Stock Solution

- Add approximately 250 mL of O_2-free distilled water to a 500-mL volumetric flask.
- Weigh and add 80 g NaOH. Dissolve using magnetic stirring. Purge top of flask with O_2-free nitrogen while dissolving.
- Weigh and add 48.0 g $Na_2S \cdot 9H_2O$ crystals that have been rinsed thoroughly with distilled water and blotted dry. Dissolve using magnetic stirring. Purge top of flask with O_2-free nitrogen while dissolving. Dilute to mark with O_2-free distilled water. Mix well.

- Transfer 250 mL of this stock solution to a second 500-mL volumetric flask.

Preparation of 1.0 g/L Polysulfide Standards

- To the first 500-mL flask, add 0.500 g sulfur.
- Dissolve using magnetic stirring at about 70°C. Purge top of flask with O_2-free nitrogen while dissolving. Cool to room temperature.
- Dilute to mark with O_2-free distilled water. Mix well.
- Transfer to 500-mL polyethylene bottle. Purge top with O_2-free nitrogen. Cover tightly. Seal cap with electrical tape. Store at room temperature.

Preparation of 3.0 g/L Polysulfide Standard

- To the second 500-mL flask, add 1.500 g sulfur.
- Dissolve using magnetic stirring at about 70°C. Purge top of flask with O_2-free nitrogen while dissolving. Cool to room temperature.
- Dilute to mark with O_2-free distilled water. Mix well.
- Transfer to a 500-mL polyethylene bottle. Purge top with O_2-free nitrogen. Cover tightly. Seal cap with electrical tape. Store at room temperature.

The simulated liquors containing 1 and 3 g/L are referred to as S-3 and S-4, respectively, in Table XVII. The comparison of analytical techniques indicates Mead amalgam, TAPPI, and UV spectrophotometric methods are more reliable than DPP. Even when DPP was conducted in the presence of $ZnCO_3$, the method did not improve. This indicates the DPP is not reliable for polysulfide sulfur analysis. Further investigations are needed to establish the reason for the unreliability of the technique. From the recovery results on simulated liquor, it is clear that the UV and TAPPI method gave better recovery results than the Mead Amalgam Method. The Mead method

has been conducted with $AgNO_3$ as titrant, as stated in the procedure of this study. The Mead Corp. has replaced $AgNO_3$ by $HgCl_2$. Table XVII shows satisfactory results were obtained with $AgNO_3$; however, the use of $HgCl_2$ may give more accurate results. Recovery tests in real liquors (S-1 and S-2) were also conducted by dissolving 3.0 and 6.0 g of elemental sulfur in a liter of WL-4 liquor. The analysis was conducted by DPP, Mead, and UV methods. The TAPPI method was avoided because of the time consumption of the technique. DPP was again proven to be unreliable. The Mead and UV methods showed good recovery, verifying the reliability of the two techniques.

TABLE XVII

POLYSULFIDE SULFUR ANALYSIS IN WHITE LIQUOR

Liquor	TAPPI[c]	Mead	UV	DPP [c]	
				with $ZnCO_3$	without $ZnCO_3$
WL-2	0.6	0.2 ± 0.2	0.6 ± 0.0	0.3	0.7
WL-3	0.1	0.4 ± 0.1	0.5 ± 0.0	0.0	0.7
WL-4	0.0	0.2 ± 0.0	0.1 ± 0.0	0.3	1.1
WL-5	0.4	1.1 ± 0.0	1.3 ± 0.0	0.6	3.6
WL-7	1.0	0.4 ± 0.0	1.1 ± 0.0	0.4	0.7
WL-8	1.6	1.3 ± 0.1	1.5 ± 0.0	0.8	1.3
S-1[a]	--	2.9 ± 0.0	2.8 ± 0.0	1.7	1.8
S-2[a]	--	5.7 ± 0.1	6.1 ± 0.0	6.7	8.2
S-3[b]	0.99	0.80 ± 0.0	1.06 ± 0.02	0.44	1.04
S-4[b]	3.11	2.64 ± 0.0	3.10 ± 0.0	2.74	3.97
Time of analysis for 1 min	120	50	1	50+[d]	50

[a]Recovery test on mill samples.
[b]Simulated liquors.
[c]Data are the result of duplicate means of $Na_2S_2O_3$ analysis before and after the addition of Na_2SO_3.
[d]The exact time depends on the successful sulfide removal from the liquor by one trial.

The suitability of the UV spectrophotometric technique as a practical analytical tool is confirmed not only by its reliability and its good reproducibility, but also by the reduced time for analysis. The times to determine polysulfide by the TAPPI, DPP (no $ZnCO_3$ added), Mead amalgam, and UV methods were estimated to be 120, 50, 50, and 1 minute, respectively. Although the analysis time was 1 minute for UV, the total analytical procedure including sample preparation, duplicate analysis, and cleaning of glassware was accomplished in 15 minutes. This is a significant time saving over any of the other methods.

In conclusion, the UV and Mead methods are reliable for polysulfide determinations in white liquor. The reliability of the TAPPI method was not fully established during this study. The DPP method was not reliable.

ANALYSIS OF SULFIDE, THIOSULFATE, AND SULFITE IN BLACK LIQUOR

The methods and techniques considered for sulfide analysis in black liquor are TAPPI T 624 ts-64, the ABC pH method, automatic potentiometric titration by Metrohm instrument, and differential pulse polarography (DPP). The TAPPI and DPP methods were investigated for thiosulfate and sulfite analysis. The principles involved with the TAPPI method, potentiometric titration, DPP, and ABC methods, as well as the principles and detailed description of the TAPPI T 625 ts-64 method, are given in Appendix V. The comparison of the methods is followed by a discussion of their reliability and the time required for analysis.

Comparison of the Methods for Sulfide, Thiosulfate, and Sulfite in Black Liquors

Sulfide Analysis

The analytical methods used for the determination of Na_2S in black liquors are the TAPPI, DPP, automatic potentiometric titration, and automatic ABC (pH) methods. These methods were compared for five weak black liquors and one oxidized

black liquor. These mill samples were identified as evaporator feed liquor. The results are shown in Table XII. There is general agreement of the sodium sulfide values by all techniques except the ABC method. The DPP with standard addition method is in better accord with the other techniques than the DPP with standard curve.

TABLE XII

BLACK LIQUOR SODIUM SULFIDE ANALYSIS BY DIFFERENT METHODS AND TECHNIQUES

Liquor	Metrohm ABC	TAPPI	Metrohm $HgCl_2$	Metrohm $AgNO_3$	DPP	
					Stand. Add.	Stand. Curve
BL-1	5.4 ± 0.2	2.9 ± 0.6	3.3 ± 0.3	2.9 ± 0.1	2.9 ± 0.2	4.0 ± 0.2
BL-2	3.3 ± 0.0	0.04 ± 0.02	0.03 ± 0.00	0.02 ± 0.01	0.08 ± 0.00	2.1 ± 0.0
BL-3	12.0 ± 0.0	8.6 ± 0.2	8.9 ± 0.2	9.0 ± 0.2	7.7 ± 0.1	14.3 ± 0.1
BL-4	6.9 ± 0.1	2.1 ± 0.1	3.4 ± 0.1	2.9 ± 0.3	2.8 ± 0.2	4.8 ± 0.1
BL-5	11.3 ± 0.1	7.5 ± 0.0	8.4 ± 0.0	8.2 ± 0.3	8.2 ± 0.2	13.7 ± 0.4
BL-6	20.9 ± 0.4	14.9 ± 0.6	15.5 ± 0.1	14.6 ± 0.0	14.5 ± 0.2	16.2 ± 0.1

For sulfide analysis in black liquor using the ABC titration, only the pH method could be considered, because the color changes of the indicators (phenolphthalein and thymolphthalein) at the end point of the titration cannot be identified in dark solutions. Table XII shows that the ABC method gave consistently higher values of sodium sulfide concentration than the other methods. This phenomenon has been previously observed by Grace et al. (52). They agree that the ABC method cannot be used for black liquor analysis. The reason for the unreliability is attributed to the buffering effect of the phenols (degradation products of lignin and extractives) and possibly to carboxylic acids (degradation products of carbohydrates).

The reliability of the TAPPI, DPP, and automatic potentiometric titration methods for sulfide analyses was verified by recovery tests. Recovery tests consist of adding a known amount of sodium sulfide to the liquor and observing which technique indicates the exact amount added. The recovery test results are shown in Table XIII. The concentration of Na_2S in liquors BL-1 and BL-6-1 are lower than expected after dilution because the recovery tests were done 2 months after the comparison tests (compare Table XII with Table XIII). The satisfactory recovery results indicate that all techniques were reliable.

TABLE XIII

BLACK LIQUOR SODIUM SULFIDE RECOVERY BY DIFFERENT METHODS

Method	Liquor	BL-1-1	BL-1-2	Recovery	BL-6-1	BL-6-2	Recovery
Metrohm $HgCl_2$		1.5 ± 0.1	2.4 ± 0.0	0.9 g/L	7.4 ± 0.1	8.4 ± 0.2	1.0 g/L
DPP[a]		1.3 ± 0.1	2.2 ± 0.0	0.9 g/L	6.2 ± 0.1	7.3	1.1g/L
TAPPI		1.4 ± 0.1	2.5 ± 0.1	1.1 g/L	6.7 ± 0.1	7.6 ± 0.1	0.9 g/L

[a]Samples for DPP analysis are diluted in 1:1 SAOB I

Sample Identification

BL-1-1: BL-1 diluted 1:1
BL-1-2: BL-1 diluted 1:1 + 1.0 g/L Na_2S
BL-6-1: Bl-6 diluted 1:1
BL-6-2: Bl-6 diluted 1:1 + 1.0 g/L Na_2S

It may be helpful to explain some of the experience with the TAPPI method. This method is a manual potentiometric titration using silver nitrate ($AgNO_3$) as titrant. The electrode response was very sluggish near the end-point region. It took as much as 45 minutes for the potential to stabilize for a single 0.1-mL increment addition. Despite the long waiting time, large potential changes were encountered at the end point. To reduce the time required for the electrode potential to reach steady state, a steady-state time of 30 seconds was selected, i.e., the electrode

potential reading was considered stable, if no change in the potential occurred within 30 seconds. The sluggish electrode potential response with $AgNO_3$ as titrant was attributed to the presence of organics and polysulfide in black liquor. Danielsen et al. (14) suggested the use of Na_2SO_3 in the liquor to eliminate the presence of polysulfide and improve the performance of the electrode response. Therefore, the addition of 5 and 10 g/L sodium sulfite to the liquor prior to testing was investigated. An improvement was observed. The total analysis time dropped from 55 to 45 minutes; and the electrode response near the end point and the potential stabilization was faster. In addition, the degree of potential change at the end point was greater using Na_2SO_3. No improvement of the electrode response and the time of analysis were observed when the amount of Na_2SO_3 was increased from 5 to 10 g/L.

By comparing the time of analysis of all methods (Table XII), it is evident that potentiometric titration using mercuric chloride as titrant is the fastest technique studied. The titration with $HgCl_2$ has an advantage of exhibiting a large and significant potential change at the end point, which was not observed when $AgNO_3$ was used. Bilberg (17,18) found the mercuric chloride titration method to be superior to the $AgNO_3$ method. This is especially the case for liquors containing organic compounds and polysulfides (17,18).

The conclusions for sulfide analysis in black liquor are as follows:

1. All tested methods and techniques are reliable except the ABC pH method.
2. The DPP (standard addition) method is recommended over the standard curve method.
3. The great disadvantage of the TAPPI procedure is its time consumption even after the improvement of the analysis time by the addition of Na_2SO_3.

4. The potentiometric titration using $HgCl_2$ is considered the best technique available. Although this consideration is based on the automatic technique, the same conclusion is considered valid for the manual technique.

Thiosulfate and Sulfite Analysis

Thiosulfate analyses were conducted by the TAPPI and DPP techniques. The results are shown in Table XIV. There appears to be a satisfactory agreement between the two methods. This is not a surprising finding, since the reaction involved in the determination of the thiosulfate by both techniques is the same and is based on the reaction $Hg^{2+} + S_2O_3^{2-} \rightarrow Hg[S_2O_3]_2^{2-}$.

TABLE XIV

BLACK LIQUOR SODIUM THIOSULFATE ANALYSIS BY DIFFERENT METHODS

Method	Liquor					
	BL-1	BL-2	BL-3	BL-4	BL-5	BL-6
DPP, No $ZnCO_3$	5.9 ± 0.2	7.5 ± 0.6	4.3 ± 0.1	4.5 ± 0.1	5.2 ± 0.2	5.2 ± 0.4
TAPPI	4.9 ± 0.2	8.1 ± 0.0	3.5 ± 0.1	4.8 ± 0.1	5.3 ± 0.2	

Recovery tests were conducted to investigate the reliability of the DPP technique by adding 1.54 g/L $Na_2S_2O_3$ to liquor BL-2 and BL-3. The liquors were tested before and after the addition of $Na_2S_2O_3$, as shown in Table XV.

The recovery tests indicated a significant difference of 16% between the added and the recovered amount. The possibility of interference by the sulfide species prompted a study to investigate the effect of sulfide removal on thiosulfate analysis. The sulfide removal was conducted by the addition of $ZnCO_3$ to all black liquors (BL-1 through 6, followed by filtration). The thiosulfate analysis was again performed by

DPP technique. Table XVI shows that sodium thiosulfate analysis is affected by sulfide presence and/or by the addition of $ZnCO_3$. Based on these results, the reliability of the DPP technique is still in question. Since thiosulfate analysis by the TAPPI method is based on the same reaction as the DPP method, the reliability of the TAPPI method requires further study.

TABLE XV

RECOVERY TEST FOR THIOSULFATE ANALYSIS BY THE DPP TECHNIQUE

Parameters	BL-3	BL-3 + 1.54 g/L $Na_2S_2O_3$	BL-2	BL-2 + 1.54 g/L $Na_2S_2O_3$
Peak potential (V)	-0.240	-0.232	-0.232	-0.224
	-0.236	-0.232	-0.228	-0.224
Peak current (NA)	1.435 EI	3.004 EI	4.049 EI	5.220 EI
	1.893 EI	3.093 EI	4.170 EI	5.060 EI
$Na_2S_2O_3$ conc. (g/L)	3.4 $\pm$ 0.0	5.2 $\pm$ 0.1	7.0 $\pm$ 0.	8.8 + 0.4

There are other methods for thiosulfate determinations. The potentiometric titration technique is described by J. Papp (16) for the determination of thiosulfate and sulfite by a using sulfide ion selective electrode. In this technique there is no need for the removal of sulfide prior to thiosulfate and sulfite analysis. The ion chromatographic method was introduced by Small et al. (28). The method is very versatile and appears to be fast (30).

Sodium sulfite analyses were conducted by the DPP and TAPPI methods. No detectable levels of sodium sulfite were found.

The reliability of the DPP and TAPPI methods for thiosulfate determination was not established during our investigation. Further study is suggested, namely, standard solutions, simulated, and real liquor evaluations to establish interference

TABLE XVI HERE

TABLE XVI

EFFECT OF $ZnCO_3$ ON THIOSULFATE ANALYSIS (g/L) BY THE DPP METHOD

Technique	BL-1	BL-2	BL-3	BL-4	BL-5	BL-6	BL-2 + 1.54 g/L $Na_2S_2O_3$	BL-3 + 1.54 g/L $Na_2S_2O_3$
)PP, no $ZnCO_3$ added	5.9 ± 0.2	7.0 ± 0.1	3.4 ± 0.1	4.5 ± 0.1	5.2 ± 0.2	5.2 ± 0.4	8.8 ± 0.4	5.2 ± 0.1
)PP, $ZnCO_3$ added	5.5 ± 0.4	6.6 ± 0.5	4.0 ± 0.2	3.6 ± 0.4	4.6 ± 0.3	5.9 ± 0.3	7.4 ± 0.1	5.7 ± 0.4

between sulfide, thiosulfate, and sulfite on thiosulfate analysis. The effect of $ZnCO_3$ for the removal of sulfide by the TAPPI procedure should also be examined. In addition, other methods and techniques should be considered, such as potentiometric titration by sulfide selective electrodes (16) and the ion chromatographic method (28,30-31).

PHASE II - EFFECT OF LIQUOR AGE AND STORAGE CONDITION ON THE STABILITY OF SULFIDE IN WHITE AND BLACK LIQUORS

SULFIDE OXIDATION IN LIQUOR ENVIRONMENTS

The sulfur species sulfide, thiosulfate, and sulfite are subject to air oxidation in the white and black liquor environments. The oxidation reactions of sulfide are considered the most important reactions occurring in the liquor environment. These are as follows:

Sulfide oxidation to thiosulfate

$$2Na_2S + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2\ NaOH$$

Sulfide oxidation to polysulfide

$$4Na_2S + O_2 + 2H_2O \rightarrow 2Na_2S_2 + 4\ NaOH$$

Sulfide oxidation in aqueous solution is a slow process (56,57), but it is accelerated by various inorganic catalysts such as Fe, Ni, and Mn sulfides (56). According to Mueller (56), Fe originates from the corrosion of mild steel, and Ni and Mn originate from the corrosion of stainless steels. Another source of Mn is wood and causticizing lime (56). These catalysts enhance oxidation of sulfide to thiosulfate (56). Polysulfide is also oxidized to thiosulfate as shown.

$$2Na_2S_2 + 3O_2 \rightarrow 2Na_2S_2O_3$$

The oxidation of sulfide to polysulfide may occur in the presence of MnO_2 (oxidizing catalyst) (57) and organic catalysts such as hydroquinone (56,58), tannins, gallic acid, pyrogallol, and activated carbon (56). The most highly selective catalysts toward polysulfide formation from sulfide are MnO_2 and activated carbon. In the presence of the organic catalysts, both thiosulfate and polysulfide may be formed. If Ni, Fe, and Mn sulfides exist in white liquor, and activated carbon is carried away from the smelt (56) (green liquor), sulfide oxidation in white liquor

leads to the formation of thiosulfate and polysulfides. The presence of these catalysts in black liquor environments indicates that polysulfide and thiosulfate can also form in black liquors.

TIME STUDIES IN WHITE LIQUOR

The instability of sulfide toward oxidation has caused difficulty in obtaining meaningful analytical results (5). This difficulty was reduced by the development of sulfide antioxidant buffers (SAOB). A time study to test the instability of sulfide ion was conducted under the following conditions.

(1) Air was excluded from the liquor by filling the sample bottle to the brim and capping.

(2) Nitrogen was purged on top of the sample.

(3) Sulfide antioxidant buffers were added to the liquor.

Three sulfide antioxidant buffers were investigated: SAOB I (8), II (5), and III (19). SAOB (I) was prepared by dissolving 80 g NaOH, 320 g sodium salicylate, and 72 g ascorbic acid in a liter of water. SAOB II was prepared by dissolving 67 g disodium EDTA, 35 g ascorbic acid, and 80 g/L NaOH in one liter. SAOB III contained 80 g/L NaOH, 40 g/L sodium salicylate, and 36 g/L ascorbic acid.

A white liquor sample was diluted (1:1) in the SAOB I, II, and III. A 25-mL aliquot of liquor was used. The samples were placed in polyethylene storage bottles and capped tightly after squeezing the bottles to expel all air present.

A fourth sample containing only the liquor was prepared by filling a polyethylene bottle completely full and capping it. A fifth sample was prepared by filling a polyethylene bottle half full, followed by a nitrogen flush over the top of the sample before the bottle was capped. Tests were run at different time intervals to

determine the levels of Na_2S. Analysis was conducted by $Cd(NO_3)_2$* (0.1M) t ration on the Metrohm automatic titrator. A 5-mL aliquot for the samples containing SAOB and a 3-mL aliquot for the samples not containing SAOB were used. Sufficient samples were prepared to allow a new sample bottle to be opened for each day of the interval tests. This prevented oxidation due to sealing and reopening a single bottle over a period of several weeks. All analytical results were made in duplicate, but only a single bottle of sample for each day, duplicating the analysis but not the storage. The samples were stored at room temperature.

The results are shown in Table XVIII. There is good agreement between the sampling procedures SAOB I, no air, and a nitrogen blanket at 0 day analysis. The deviation from this agreement by SAOB II and III suggests a possible interference in sulfide determination. The results also show that sampling and storing the liquor in SAOB I is the best procedure tested. However, from the corrosion standpoint the addition of SAOB I to the liquor will lead to a change in the composition of the liquor. The change will cause misleading interpretation of the corrosion data. Thus, the use of a nitrogen blanket or air is recommended in sampling white liquor for corrosion studies. In addition, the maximum storage time of the liquor sample is one week. As can be seen from Table XVIII, within one week of storage time, the loss in sulfide ion determined by nitrogen and no air sampling is comparable to the loss observed when the liquor was stored in SAOB I for one week.

TIME STUDIES IN WEAK BLACK LIQUOR

The time studies for weak black liquor were conducted under the following storage methods.

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[a] $Cd(NO_3)_2$ was used instead of $HgCl_2$, because the latter reacts with ascorbic acid, an ingredient of SAOB.

- Air exclusion from the liquor by filling the sample bottle to the brim, capping, and sealing with electrical tape.
- Filling a bottle approximately 2/3 full, covering tightly but not sealing the cap.
- Filling a bottle approximately 2/3 full, purging with nitrogen, covering the bottle, and sealing with electrical tape.

For this study, fresh weak black liquor from the digester was obtained from a nearby mill. The liquor was then transferred to smaller bottles and stored under the above conditions at room temperature. Sulfide analysis was conducted by manual potentiometric titration using $HgCl_2$ as a titrant. The results are shown in Table XIX. The results indicate that sulfide concentration in black liquor remains stable for 14 days when the liquor is stored under the condition of no air and under a nitrogen blanket.

TABLE XVIII

EFFECT OF LIQUOR AGE AND STORAGE METHOD (METHOD OF TRANSFER) ON THE CHANGES OF SULFIDE CONCENTRATION IN WHITE LIQUOR

Method of Transfer	Days			
	0	4	7	14
Antioxidants				
SAOB I	30.7 ± 0.7	30.4 + 0.5	30.2 ± 0.65	29.5 ± 0.5
SAOB II	27.4 ± 0.05	27.2 ± 0.0	27.1 ± 0.1	27.1 ± 0.1
SAOB III	33.2 ± 1.15	31.8 ± 1.05	30.4 ± 0.8	31.0 ± 0.6
No air	30.2 ± 0.5	29.0 ± 0.05	29.4 ± 0.05	28.4 ± 0.1
Nitrogen blanket	30.2 ± 0.5	29.9 ± 0.2	29.6 ± 0.05	28.6 ± 0.1

TABLE XIX

EFFECT OF LIQUOR AGE AND STORAGE METHOD (METHOD OF TRANSFER) ON SULFIDE CONCENTRATION IN BLACK LIQUOR

Method of Transfer	Days					
	0	1	2	7	10	14
No air	11.4 ± 0.0	11.6 ± 0.1	11.5 ± 0.1	11.3 ± 0.1	11.4 ± 0.2	11.6 ± 0.2
Air capped	11.4 ± 0.0	11.6 ± 0.2	11.7 ± 0.0	11.5 ± 0.0	11.4 ± 0.2	10.7 ± 0.1
Nitrogen blanket	11.4 ± 0.0	11.7 ± 0.3	11.6 ± 0.1	11.6 ± 0.1	--	11.3 ± 0.1

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APPENDIX I

PREPARATION OF ANALYTICAL REAGENTS/INDICATORS

Scope

- This procedure describes the preparation of reagents and indicators used in the analyses of sulfur species compounds in kraft white and weak black liquors. The procedure contains only those reagents and indicators used in various analytical methods pertaining to Project 2926-56.
- In preparing liquid reagents, indicators, solutions, and buffers, use analytical grade chemicals and distilled water.

Indicators

- Eriochrome Black T
  - Mix together 0.5 g dye and 100 g NaCl to prepare a dry powder mixture.
- Phenolphthalein, 0.1%
  - Dissolve 0.1 g in 100 mL of 50-70% ethanol or methanol. Since this solution will be slightly acid, neutralize it by adding 0.1N NaOH cautiously until a faint pink color appears, then just remove the color with a drop or two of 0.1N HCl.

Liquid Reagents

- Acetic Acid, Glacial, 2:5
  - To a 500-mL volumetric flask containing about 250 mL of distilled water, slowly and cautiously add 200 mL of concentrated glacial acetic acid. Dilute to mark with distilled water and mix well. The preparation of this solution should be performed under a ventilation hood.
- Ammoniacal Silver Nitrate
  - Prepare a 2.5% solution by weighing and adding 2.5 g $AgNO_3$ to 100 mL of distilled water in a 150-mL beaker. Place on a magnetic stirrer and stir using a Teflon-covered magnetic stirring bar. After the $AgNO_3$ is

dissolved, continue stirring and slowly add concentrated NH_4OH dropwise until the brown precipitate just clears. Transfer the solution to a dark-colored, glass-stoppered bottle.

- Ammonium Hydroxide, 1:99
  - By means of a 1-mL transfer or measuring pipette, transfer 1 mL of concentrated ammonium hydroxide to a 100-mL volumetric flask and dilute to mark. Mix well.
- Barium Chloride, 10%
  - Dissolve 100 g of $BaCl_2 \cdot 2H_2O$ in about 200 mL distilled water in a 1000-mL volumetric flask and dilute to mark.
- Hydrochloric Acid, 6N
  - To a 150-mL beaker containing 50 mL of distilled water, slowly and cautiously add 50 mL of concentrated HCl, stirring frequently. Transfer to a suitable storage container.
- Hydrochloric Acid, 0.1N
  - To a 100-mL volumetric flask containing about 75 mL of distilled water, add 1 mL of concentrated HCl. Dilute to mark with distilled water and mix.
- Sodium Carbonate, Saturated
  - For a saturated Na_2CO_3 solution at 25°C, dissolve 33.4 g Na_2CO_3 in 200 mL of distilled water. A hot plate and magnetic stirrer will aid in preparation of the solution.
- Sodium Carbonate, 1M
  - Dissolve 106 g Na_2CO_3 in a 1000-mL volumetric flask containing about 300 mL distilled water. Dilute to mark with distilled water and mix well.

- Sodium Hydroxide, 0.2M
  - Dissolve 8.0 g NaOH in a 1000-mL volumetric flask containing about 200 mL distilled water. Dilute to mark with distilled water and mix well. Transfer to a polyethylene storage bottle.
- Sodium Hydroxide, 4M
  - Dissolve 160 g NaOH in a large Erlenmeyer flask or other suitable vessel containing about 400 mL of distilled water. Allow to cool in a cold-water bath. Transfer to a 1000 mL volumetric flask, dilute to mark with distilled water, and mix well. Transfer to a polyethylene storage bottle.
- Sodium Hydroxide, 12M
  - Dissolve 480 g NaOH in a large Erlenmeyer flask or other suitable vessel containing about 500 mL of distilled water. Allow to cool in a cold-water bath. Transfer to a 1000-mL volumetric flask. Dilute to mark with distilled water and mix well. Transfer to a polyethylene storage bottle.
- Sodium Hydroxide, 20%
  - Dissolve 200 g NaOH in a large Erlenmeyer flask or other suitable vessel containing about 500 mL of distilled water. Allow to cool in a cold-water bath. Transfer to a 1000-mL volumetric flask. Dilute to mark with distilled water and mix well. Transfer to a polyethylene storage bottle. (Caution: The preparation of sodium hydroxide solutions involves a highly exothermic reaction capable of generating a harmful degree of heat. Care must be taken in handling these solutions to prevent injury.)

- Sodium Chloride, 3M in 10^{-2}M NaOH, Oxygen-free
  - Dissolve 175.5 g NaCl and 0.4 g NaOH in about 500 mL of distilled water in a 1000-mL volumetric flask. Dilute to mark with distilled water. Purge for 1 hr with O_2-free nitrogen. Stopper and seal with parafilm.
- Sulfuric Acid, dilute 20%
  - Into 800 mL of distilled water, cautiously pour 200 mL of concentrated H_2SO_4, using constant stirring.
- Zinc Sulfate, 1M
  - Dissolve 287 g of $ZnSO_4 \cdot 7H_2O$ in a 1000-mL volumetric flask containing about 400 g of distilled water. Dilute to mark with distilled water and mix well.

Standard Solutions

- EDTA, 0.1M
  - Dissolve 37.23 g EDTA (disodium ethylenediamine tetraacetate dihydrate, $Na_2H_2C_{10}H_{12}O_8N_2 \cdot 2H_2O$) in a 1000-mL volumetric flask containing about 200 mL of distilled water. Dilute to mark with distilled water and mix well.
- Mercuric Chloride, 0.05M
  - Dissolve 13.5748 g $HgCl_2$ in a 1000 mL volumetric flask containing about 200 mL of distilled water. Dilute to mark and mix well. The exact molarity may be determined by the equation:

$$\text{Molarity } HgCl_2 = \frac{\text{wt. } HgCl_2 \times 0.0500M}{13.5748 \text{ g}}$$

Caution: Never oven dry $HgCl_2$. It is deadly poisonous.

• Mercuric Chloride, 0.1000M

- Dissolve approximately 27.1496 g $HgCl_2$ in a 1000-mL volumetric flask containing about 200 mL distilled water. Dilute to mark with distilled water and mix well. Determine the exact molarity from the equation:

$$\text{Molarity } HgCl_2 = \frac{\text{wt. } HgCl_2 \times 0.1000M}{27.1496 \text{ g}}$$

Caution: Never oven dry $HgCl_2$. It is deadly poisonous.

• Silver Nitrate, 0.1000N

- Dissolve 16.9873 g $AgNO_3$ in a 1000-mL volumetric flask containing about 200 mL of distilled water. Dilute to mark with distilled water and mix well. Transfer to a dark-colored glass-stoppered bottle. Determine the exact normality from the equation:

$$\text{Normality } AgNO_3 = \frac{\text{wt. } AgNO_3 \times 0.1000N}{16.9873 \text{ g}}$$

Buffer

• Acetate Buffer, 0.5M

- Dissolve 41.0 g $NaC_2H_3O_2$ in approximately 300 mL of distilled water in a 1000-mL volumetric flask. Add 40 mL glacial acetic acid. Dilute to mark with distilled water and mix well.

• Acetate Buffer for Na_2SO_3 solutions

- Dissolve 20.6 g $NaC_2H_3O_2$ in a 100-mL volumetric flask containing about 40 mL of distilled water. Add 20 mL of glacial acetic acid. Dilute to mark with distilled water and mix well. For each 10 mL of Na_2SO_3 solution desired, add 1 mL of acetate buffer.

• Buffer No. 2

1 Dissolve 1.179 g disodium salt of ethylenediamine tetraacetate dihydrate (EDTA) and 780 mg $MgSO_4 \cdot 7H_2O$ or 644 mg $MgCl_2 \cdot 6H_2O$ in 50 mL of distilled water.

2. Add this solution to 16.9 g NH_4Cl and 143 mL concentrated NH_4OH with mixing and dilute to 250 mL with distilled water.

3. Transfer to a polyethylene storage bottle.

• SAOB* I

1. Dissolve 40 g NaOH in a 500-mL volumetric flask containing about 200 mL of distilled water. Cool to room temperature.

2. Purge with O_2-free nitrogen for 15 minutes. Stopper immediately upon removal of purging apparatus.

3. Quickly add 160 g sodium salicylate with a funnel and glass stirring rod. Stopper. Dissolve sodium salicylate.

4. Quickly add 36 g ascorbic acid with a funnel and glass stirring rod. Stopper. Dissolve the ascorbic acid.

5. Dilute to mark with O_2-free distilled water.

6. The solution should be straw-colored. If the solution becomes dark brown, it must be discarded.

• SAOB* II

1. Dissolve 80 g NaOH in a 1000-mL volumetric flask containing about 400 mL of distilled water. Cool to room temperature.

2. Purge with O_2-free distilled water for 15 minutes. Stopper immediately upon removal of purging apparatus.

3. Add 67 g of disodium EDTA with a funnel. Stopper. Dissolve EDTA.

4. Add 35 g of ascorbic acid with a funnel. Stopper immediately. Dissolve ascorbic acid.

*Sulfide antioxidant buffers.

5. Dilute to mark with O_2-free distilled water. Mix well.
6. Discard solution if it becomes dark brown in color.

• SAOB* III

1. To a 1000-mL volumetric flask containing about 250 mL of distilled water, add 80 g NaOH and dissolve. Allow to cool to room temperature. Purge with O_2-free nitrogen for 15 minutes, then quickly stopper.
2. Add 40 g of sodium salicylate with a funnel and glass stirring rod. Quickly stopper. Dissolve the sodium salicylate.
3. Add 36 g of ascorbic acid with a funnel and glass stirring rod. Quickly stopper, then dissolve the ascorbic acid.
4. Dilute to mark with O_2-free distilled water. Quickly stopper and mix well.
5. Discard the solution if it becomes dark brown in color.

Miscellaneous

• Sodium amalgam

1. Transfer 100 to 200 mL of mercury to a 600-mL plastic beaker.
2. Add 200 mL of saturated Na_2CO_3 solution.
3. Place one platinum electrode in the mercury layer and attach to the negative terminal of a dc power supply (4 to 6 amperes). Be sure to insulate the electrode from the carbonate solution.
4. Place a second platinum electrode midway in the carbonate solution (avoiding any contact with the mercury). Connect this electrode to the positive terminal.
5. Electrolize 4-6 hours, using 4 to 6 amperes.
6. Separate the mercury-electrolyte phases by decantation and rinse the amalgam several times with distilled water.

*Sulfide antioxidant buffers.

7. Store the washed amalgam under a layer of distilled water in a vented bottle.

- Zinc Amalgam + Vanadous Chloride Polarographic Scrubbing

1. Zinc Amalgam. Place about 10 g of granular zinc into a beaker. Cover with deionized water. Add two drops of concentrated HCl. Add the volume of mercury necessary to create an amalgam that is free from an excess of liquid mercury.
2. Vanadous Chloride. In a 400-mL beaker, boil two grams of ammonium metavanadate with 25 mL of concentrated hydrochloric acid and dilute with distilled water to 250 mL. The solution produced is usually blue or green and contains vanadium in various higher oxidation states.
3. Transfer the vanadous chloride solution to a gas scrubbing tower. Add the amalgamated zinc to this solution (which reduces the vanadium to the +2 state upon passing nitrogen through the solution) until a clear violet color is obtained.

STANDARDIZATION OF ANALYTICAL REAGENTS

STANDARDIZATION OF 50 g/L Na_2S in 1:1 SAOB AGAINST CADMIUM NITRATE

Scope

- This procedure describes a method of standardizing a stock solution of 50 g/L sodium sulfide that has been prepared in 1:1 SAOB.
- The 50 g/L Na_2S stock solution may then be subsequently diluted to obtain standards for sulfide analysis using differential pulse polarography.

Apparatus

- pH meter with a millivolt scale
- 50-mL burette and burette stand

- Orion 94-16A sulfide-ion selective and Orion 90-02 double junction reference electrodes.
- Magnetic stirrer and a Teflon-covered magnetic stirring bar
- 150-mL and 250-mL beakers
- 5-mL, 10-mL, and 50-mL transfer pipettes

Reagents/Chemicals

- SAOB I
- 0.1N $Cd(NO_3)_2$ Standard
- $Na_2S \cdot 9H_2O$ crystals

Preparation of 50 g/L Na_2S Stock Solution

- Pipette 50 mL of SAOB I into a 150-mL beaker.
- Add 15.4 g $Na_2S \cdot 9H_2O$ crystals that have been thoroughly washed with distilled water and blotted dry with filter paper. This should be done beneath a ventilation hood.
- Dissolve the crystals using magnetic stirring.
- Quantitatively transfer this solution to a 100-mL volumetric flask.
- Dilute to mark with distilled water, stopper, and mix well.

Standardization

- Pipette 10 mL of SAOB I into a 250-mL beaker.
- Dilute to 100 mL with distilled water.
- Place a Teflon-covered magnetic stirring bar into the beaker.
- Place the beaker on a magnetic stirrer and adjust the rate of stirring short of creating a vortex in the liquid.
- Pipette 5 mL of 50 g/L Na_2S stock solution into the beaker. Lower the electrodes into the solution and record the initial millivolt reading.
- Titrate the sample potentiometrically with 0.1000N $Cd(NO_3)_2$ using fixed increment additions. Record the steady emf after each increment addition.

A large and fairly sudden change in emf will occur at end point. Continue the titration with two more increment additions, then stop the titration.

Data/Calculation

- Record the volume increments and their corresponding millivolt readings in columnar fashion.
- Plot the data points on linear graph paper, with titrant volume on the abscissa and millivolts on the ordinate.
- Connect the two points bordering the largest millivolt change with a straight-edge ruler. Measure the straight-line length, divide the measurement by two and mark this point, then note the corresponding volume on the abscissa and record.

$$\text{g/L } Na_2S = \frac{\frac{\text{Normality } Cd(NO_3)_2}{1000 \text{ mL}} \times \text{mL } Cd(NO_3)_2 \times 78.04 \text{ g/eq}}{0.005 \text{ L sample}}$$

STANDARDIZATION OF IODINE SOLUTION AGAINST SOLID ARSENIC TRIOXIDE

Scope

- The titration of iodine solution against solid arsenic trioxide is one laboratory method which may be used to standardize iodine solutions. Iodine solutions are not stable and must stand for several days to allow for complete dissolution before standardization.
- The standardization of iodine is necessary for analysis of sulfur species in kraft liquor according to TAPPI STANDARD T 624 os-68, "Analysis of Soda and Sulfate White and Green Liquors."

Apparatus

- Analytical balance
- Spatula for transfer of chemicals in weighing

- 50-mL burette and burette stand
- Small funnel for filling burette
- (3) 250-mL Erlenmeyer flasks

Reagents/Indicators

- Primary standard grade As_2O_3 that has been dried for 1 hour at 110°C.
- Approximate 0.2N I_2 solution
- 1N NaOH
- 6N HCl
- $NaHCO_3$
- Phenolphthalein
- Thyodene as a starch indicator

Procedure

- Preparation of As_2O_3 solution
  - With the analytical balance, determine the empty mass of the Erlenmeyer flask and record.
  - Add 0.2 g As_2O_3 into each flask. Record mass.
  - Add 2 mL 5N NaOH (or 10 mL 1N NaOH) to each flask. Dissolve.
  - Dilute to the 75-mL mark with distilled water.
  - Add 2 drops phenolphthalein. This turns the solution red and indicates a basic pH.
  - Add 6N HCl until red color disappears. Add 1 mL to excess.
  - Add 3-4 g $NaHCO_3$ to buffer the solution. The $NaHCO_3$ must be added slowly at first to avoid loss of solution due to effervescence of CO_2.
  - Add thyodene (1 or 2 spatulas) as an iodine indicator.
- Titration
  - Check cleanliness of burette by rinsing with distilled water. Any droplets on inner surface indicate an unclean burette.

- Rinse burette with iodine solution three times by adding and draining approximately 10 mL iodine solution.
- Fill burette with iodine solution. Drain air bubbles from burette tip. Refill. Record initial burette volume.
- Titrate until the first faint purple or blue color that lasts for 30 sec or more. Record final burette reading.

Data/Calculations

- Record data as follows:

	Trial A	Trial B	Trial C
Mass of flask			
Mass of flask + As_2O_3			
Mass of As_2O_3			
Burette I_2 initial			
Burette I_2 final			
Volume I_2			

- Calculation

$$N\ I_2 = \frac{\frac{\text{wt. } As_2O_3}{49.455\ \text{g/eq}}}{\text{Vol. } I_2}$$

STANDARDIZATION OF 0.2M Na_2SO_3 BY ACIDIC IODINE TITRATION

Scope

- This procedure describes a method of standardization of a stock solution of 0.2M Na_2SO_3 by acidic iodine titration.
- The standardization procedure is an adaptation of the "S.F.R.C.b" determination in TAPPI T 624 os-68.

- The sodium sulfite stock solution may be used for serial dilutions to obtain sulfite standards for DPP determinations of sodium sulfite in kraft white or weak black liquors.
- Sodium sulfite solutions are not stable and must be standardized each day prior to use.

Apparatus

- 50-mL burette and burette stand
- 1000-mL volumetric flask
- 25-mL graduated cylinder
- 5-mL, 20-mL, and 50-mL transfer pipettes
- (3) 250-mL Erlenmeyer flasks

Reagents/Indicators

- 0.1N $Na_2S_2O_3$ Standard
- 0.2N I_2 Standard
- 20% H_2SO_4
- Acetic acid, glacial
- Sodium acetate, c.p.
- Analytical grade Na_2SO_3
- Thyodene as a starch indicator

Preparation of 0.2M Na_2SO_3 Stock Solution

- Add about 200 mL of distilled water to a 1000-mL volumetric flask.
- Weigh and add 20.5 g $NaC_2H_3O_2$. Dissolve the sodium acetate completely by swirling the contents of the flask.
- Add 20 mL of glacial acetic acid. (The sodium acetate crystals should be completely dissolved before adding the glacial acetic acid.)
- Weigh and add 25.2 g Na_2SO_3 to the flask and dissolve.
- Dilute to mark with distilled water and mix well.

Procedure

- Pipette 5 mL of 20% H_2SO_4 into a 250-mL Erlenmeyer flask.
- Pipette 50 mL of 0.2N iodine solution into the flask.
- Pipette 20 mL of 0.2M Na_2SO_3 stock solution into the flask while vigorously swirling the contents of the flask.
- Titrate the excess iodine with 0.1N $Na_2S_2O_3$. When the iodine becomes faint yellow, add 1 or 2 microspatulas of thyodene. The solution becomes purple. Continue the titration dropwise. At end point, one drop of 0.1N $Na_2S_2O_3$ will turn the solution from purple to clear. It requires approximately 20 mL of 0.1N Na_2SO_3. Record the equivalent volume.
- Perform the titration in triplicate.

Calculations

- Molarity $Na_2SO_3 = \frac{[(mL\ I_2 \times N I_2) - (mL\ Na_2S_2O_3 \times N\ Na_2S_2O_3)]}{mL\ Na_2SO_3} \times \frac{1}{2}$
- g/L Na_2SO_3 = Molarity Na_2SO_3 x 126.04

STANDARDIZATION OF SODIUM THIOSULFATE AGAINST STANDARD IODINE

Scope

- This procedure describes the method used in the standardization of sodium thiosulfate using standardized iodine as titrant.
- The standardized $Na_2S_2O_3$ solution is subsequently used in analysis of sulfide content using TAPPI STANDARD T 624 os-68.

Apparatus

- Analytical balance
- 50-mL burette and burette stand
- 5 and 20-mL transfer pipettes
- (3) 250-mL Erlenmeyer flasks

- 2000-mL volumetric flask
- Small funnel for filling burette

Chemicals/Reagents/Indicators

- Reagent grade $Na_2S_2O_3 \cdot 5H_2O$
- Standardized iodine solution
- Thyodene as starch indicator
- 20% H_2SO_4

Procedure

- Preparation of approximately 0.1N sodium thiosulfate
  - Dissolve 50 g $Na_2S_2O_3 \cdot 5H_2O$ in 400 mL of distilled water.
  - Dilute to mark. Cover with glass stopper.
- Standardization
  - Rinse burette three times with 5-10 mL of thiosulfate solution.
  - Fill burette to above the zero mark. Drain to the zero mark. Record initial volume.
  - Pipette 20 mL iodine solution into an Erlenmeyer flask.
  - Acidify with 5 mL 20% H_2SO_4.
  - Titrate until iodine solution becomes faint yellow.
  - Add 1 or 2 microspatula(s) of thyodene.
  - Titrate to end point (one drop purple to clear).
  - Record final burette reading.

Calculation

- Normality $Na_2S_2O_3 = \frac{\text{Vol. } I_2 \times \text{Normality } I_2}{\text{Vol. } Na_2S_2O_3}$

STANDARDIZATION OF 0.51N HCl

Scope

- This procedure utilizes a solution of standard NaOH which has been standardized with KHP (potassium acid phthalate).
- Standard HCl is subsequently used in determination of sodium sulfide by the ABC titration method.

Apparatus

- 10-mL burette and burette stand
- (6) 125-mL Erlenmeyer flasks
- Analytical balance
- 500-mL volumetric flask with rubber stopper
- 2000-mL volumetric flask
- 100-mL transfer and 10-mL measuring pipettes

Chemicals

- Reagent grade potassium acid phthalate
- Reagent grade sodium hydroxide
- Reagent grade concentrated HCl
- Phenolphthalein as indicator

Procedure

- Preparation of approximately 0.5N NaOH
  - Add about 100 mL distilled water to the 500-mL volumetric flask.
  - Weigh a dry beaker. Quickly weigh approximately 10 g NaOH. Immediately transfer to the volumetric flask containing about 100 mL distilled water. Dissolve NaOH in flask with a rapid swirling motion. Dilute to mark.
- Preparation of KHP
  - With an analytical balance, accurately weigh between 1.0000 to 1.2000 g of KHP into each of three 125-mL Erlenmeyer flasks and recording each mass.

- Add about 30 mL of distilled water and dissolve. Warming the flasks slightly may be necessary for dissolving.

• Standardization of NaOH

- Rinse 10-mL burette three times with 1 to 2 mL NaOH.
- Fill burette with unstandardized NaOH.
- Record initial burette volume.
- Add 1 or 2 drops phenolphthalein.
- Titrate to endpoint (colorless to pink) and record final volume. Repeat with remaining flasks.
- Calculate normality of NaOH.

• Preparation of approximately 0.5$\underline{1}$N HCl

- With 100-mL and 10-mL measuring pipettes, transfer 101.9 mL concentrated hydrochloric acid to 2000-mL volumetric flask that has been previously filled with about 1000 mL of distilled water. Swirl contents of flask while adding HCl.
- Dilute to mark and insert ground glass stopper. Mix well.

• Standardization of HCl

- Refill 10-mL burette containing the standard NaOH. Drain to the zero mark. Record initial volume.
- With a 5-mL pipette, transfer HCl solution to each of three 125-mL Erlenmeyer flasks.
- Add 1 or 2 drops phenolphthalein.
- Titrate to end point (pink to colorless). Record final volume.

Calculations

• Normality NaOH = $\dfrac{\dfrac{\text{wt. KHP}}{204.2\ \text{g/mole}}}{\text{Vol. HCl}}$

- Normality HCl = $\frac{\text{Normality NaOH x Vol. NaOH}}{\text{Vol. HCl}}$

STANDARDIZATION OF CADMIUM NITRATE AGAINST EDTA

Scope

- This procedure describes the standardization of 0.1N $Cd(NO_3)_2$ against a primary standard of 0.1N EDTA using Eriochrome Black T as an end point indicator.
- Standardized cadmium nitrate is subsequently used for standardization of sulfide stock solutions containing SAOB and for sodium sulfide analyses of kraft white liquors.

Apparatus

- Analytical balance
- Spatula for transfer of chemicals in weighing
- 50-mL burette and burette stand
- Small funnel for filling burette
- (3) 250-mL Erlenmeyer flasks
- 1000-mL volumetric flask
- 2-mL and 25-mL transfer pipettes

Reagents/Chemicals

- 0.1000N EDTA Primary Standard
- Buffer No. 2
- $Cd(NO_3)_2 \cdot 4H_2O$
- Eriochrome Black T indicator

Preparation of 0.1N $Cd(NO_3)_2$

- Add about 200 mL of distilled water to a 1000-mL volumetric flask.
- Weigh and add 30.8 g $Cd(NO_3)_2 \cdot 4H_2O$ to the flask.

• Dissolve the crystals and dilute to mark with distilled water. Mix well.

Standardization

• Rinse the 50-mL burette three times with 5-10 mL of 0.1N EDTA.

• Fill the burette with 0.1N EDTA. Expel air bubbles from the burette tip. Drain to the 0.00-mL mark.

• Run a blank of Buffer No. 2 to test the magnesium sulfate content for proper end point determination. This volume will later be subtracted from the equivalent volume of EDTA during the standardization of cadmium nitrate.

  - Add 25 mL of distilled water to a 250-mL Erlenmeyer flask.
  - Pipette 2 mL of Buffer No. 2 into the flask.
  - Add 1 microspatula of Eriochrome Black T indicator. The addition of indicator should yield a pink or light wine-red color.
  - Add EDTA from the burette dropwise. The solution must turn blue within a few drops addition of EDTA; if not, there is insufficient $MgSO_4 \cdot 7H_2O$ content in Buffer No. 2. Record the mL volume EDTA to approximately $\pm$ 0.01 mL and record as the blank correction factor.
  - Refill the burette and drain to the burette zero mark.

• Standardization of cadmium nitrate

  - Add about 75 mL of distilled water to a 250-mL Erlenmeyer flask.
  - Pipette 25 mL of approximately 0.1N $Cd(NO_3)_2$ into the flask.
  - Pipette 2 mL of Buffer No. 2 into the flask.
  - Add 1 microspatula of Eriochrome Black T indicator.
  - Titrate to end point. The solution will initially be wine-red in color.
  - The transition color is purple. At end point, one drop of EDTA titrant will turn the solution to blue. Record equivalent volume.

Calculation

- Normality $Cd(NO_3)_2$ = $\frac{\text{Normality EDTA x (Volume EDTA - mL blank)}}{\text{Volume } Cd(NO_3)_2}$

APPENDIX II

CALCULATION OF Na_2S, $Na_2S_2O_3$, and Na_2SO_3 IN TAPPI T 624 os-68

The chemical reaction involved in the determination of the Total Reducing Compound "T.R.C.," and sulfide-free reducing compounds "S.F.R.C.$_b$" and "S.F.R.C.$_c$" are as follows:

"T.R.C."

$$S^{2-} + I_2 \rightleftarrows S + 2I^- \quad (1)$$

$$SO_3^{2-} + I_2 + H_2O \rightleftarrows SO_4^{2-} + 2I^- + 2H^+ \quad (2)$$

$$2S_2O_3^{2-} + I_2 \rightleftarrows S_4O_6^{2-} + 2I^- \quad (3)$$

"S.F.R.C.$_b$"*

$$SO_3^{2-} + I_2 + H_2O \rightleftarrows SO_4^{2-} + 2I^- + 2H^+ \quad (2`)$$

$$2S_2O_3^{2-} + I_2 \rightleftarrows S_4O_6^{2-} + 2I^- \quad (3`)$$

"S.F.R.C.$_c$"

$$IO^- + SO_3^{2-} \rightleftarrows SO_4^{2-} + I^- \quad (4)$$

$$4IO^- + S_2O_3^{2-} + H_2O \rightleftarrows SO_4^{2-} + 4I^- + H^+ \quad (5)$$

Let a, b, and c represent the molar concentrations of sulfide, sulfite, and thiosulfate. The number of equivalents/liter of iodine used to complete the reactions (1-3), (2`- 3`), and (4-5) are,

"T.R.C." (1) = 2a (2) = 2b (3) = c

"S.F.R.C.$_b$" (2`) = 2b (3`) = c

"S.F.R.C.$_c$" (4) = 2b (5) = 8c

The number of equivalents of iodine is equal to 2 and 8 for sulfite and thiosulfate, respectively. According to the following equation,

$$I_2 + H_2O \rightleftarrows HIO + I^- + H^+$$

*The dash (`) is added to the equation numbers to differentiate the "T.R.C." from "S.F.R.C.$_b$" steps.

two equivalents of iodine ($I_2 = 2I$) are needed to generate one HIO (or IO^-). This means that 2 equivalents of iodine are needed to form one IO^- to complete reaction (4). By the same token, 8 equivalents of iodine are needed to form 4 IO^- to complete reaction (5).

Assume that x, y, and z are the net equivalents/liter of iodine used in steps "T.R.C.," "S.F.R.C.$_b$" and "S.F.R.C.$_c$." Then, from Eq. (1-3)

$$2a + 2b + c = x$$

and from Eq. (2`- 3`)

$$2\,b + c = y$$

and from Eq. (4-5)

$$2\,b + 8\,c = z$$

Then by simple mathematical manipulations, the quantities a, b, and c may be derived.

$$a = \frac{x - y}{2} \tag{6}$$

$$b = \frac{z - 8c}{2} \tag{7}$$

$$c = \frac{z - y}{7} \tag{8}$$

By substituting for x = "T.R.C.," y = "S.F.R.C.$_b$," and z = "S.F.R.C.$_c$," a = Na_2S in g/L, b = Na_2SO_3 in g/L, and c = $Na_2S_2O_3$ in g/L in the Eq. (6-8), the calculations for the TAPPI method are derived as shown below.

$$Na_2S\ g/L = \frac{(\text{"T.R.C."} - \text{"S.F.R.C.}_b\text{"})}{2} \times 78.1$$

$$\text{Na } SO_2 \text{ g/L} = \frac{\text{"S.F.R.C.}_c\text{"} - \left(\frac{Na_2S_2O_3 \times 8}{158.1}\right)}{2} 126.1$$

$$Na_2S_2O_3 \text{ g/L} = \frac{(\text{"S.F.R.C.}_c\text{"} - \text{"S.F.R.C.}_b\text{"})}{7} 158.1$$

The numbers 78.1, 126.1, and 158.1 are the molecular weights of Na_2S, Na_2SO_3, and $Na_2S_2O_3$, respectively.

APPENDIX III

EQUIPMENT COST ANALYSIS

Date & ref.

Apparatus	Manufacturer	Cost
PAR Model 384-1 polarographic system	EG & G Princeton Applied Research	$10,700.00
Metrohm E636 Titroprocessor, E649 magnetic stirrer & E635 titrating stand	Brinkman Instruments	14,500.00
Mettler DL40 MemoTitrator	Mettler Instrument Corp.	8,925.00
Mettler GA 40 printer	Mettler Instrument Corp.	1,025.00
Gilson Pipetman P200 microliter pipet	Rainin Instrument Co.	139.50
RC 20 Pipet tips, 0-200 µL, yellow, pkg 1000	Rainin Instrument Co.	35.00
94-16A sulfide-ion selective electrode	Orion Research Inc.	191.00
90-02 Double-junction reference electrode	Orion Research Inc.	80.75
94-48 Cadmium electrode	Orion Research Inc.	60.00
EA246 Silver billet electrode (combination)	Brinkman Instruments, Inc.	73.00
EA120 Glass electrode	Brinkman Instruments, Inc.	72.00
No. 476060 Platinum electrode	Corning Glass Works	65.00
No. 476002 Saturated calomel electrode	Corning Glass Works	35.00
Model ST576 spectrophotometer (1977, obsolete)	Perkin-Elmer	16,700.00

APPENDIX IV

POTENTIOMETRIC METHODS

INTRODUCTION AND PRINCIPLES

Potentiometric methods involve the determination of a potential difference between two electrodes immersed in the solution to be analyzed. The potential difference is often referred to as all potential, emf., or simply, potential. The electrodes consist of an ion-selective electrode and a double junction reference electrode. Since the potential of the reference electrode is constant, the changes in the potential difference are due to changes in the potential of the ion-selective electrode. The changes in the potential difference are related to the ion activity of the tested species by the Nernst equation.

$$E = E^\circ + 2.3 \frac{RT}{nF} \log A$$

Here, E is the potential difference between the electrodes, E° is the standard potential, R is the universal gas constant, T is the temperature, n is the charge on the ion, F is the Faraday constant, and A is the activity of the ion. The activity is related to the ion concentration by the following equation.

$$A = \gamma C$$

where C is the concentration and γ is the activity coefficient for the ion. The activity coefficient is a function of the total ionic strength of the solution. By controlling the total ionic strength of the solution and therefore fixing the activity coefficient, the ion-selective electrode potential response (or potential difference of the two electrodes) can be directly related to the ion concentration.

The Importance of the Ionic Strength Adjustment Buffer (NaOH)

The ionic strength can be controlled by using an ionic strength adjustment buffer (ISAB) containing a noninterfering ionic species. The ISAB used for our sulfide analysis was 20% by weight NaOH. The addition of 20% NaOH has two advantages: (1) it controls the ionic strength of the solution, and (2) it increases the pH of the solution. The increase in pH is very important to the proper analysis of all the sulfide ions present in the solution. Since the sulfide-selective electrode responds only to the sulfide ion present in the form of S^{2-}, the pH of the solution must be raised to approximately 14 to ensure the existence of the sulfide ion in S^{2-} form and not HS^- and H_2S forms.

Type of Potentiometric Methods

Potentiometric methods consist of three types: direct potentiometric method, incremental method, and potentiometric titration.

The direct potentiometric method requires a single potentiometric or potential measurement on the sample solution. The sample's potential (emf.) measurement is compared with a previously prepared calibration curve or to the sample concentration or activity read directly from a calibrated meter scale. Direct measurements are useful where samples are essentially pure solutions of the ion tested or have a relatively higher constant total ionic strength.

Two incremental methods are known - the known addition and analate addition. In the known addition technique, a small volume of a known concentration of the ion being measured is added to a large volume (about 100 fold) of the unknown sample. The total concentration of the sample is calculated from the change in potential difference before and after adding the known increment. This method, unlike direct measurments, does not require preparation of a calibration curve.

Analate addition is the reverse of the known addition method where the sample is added to a 50 to 100-fold excess of a known reagent solution. The reagent solution contains the necessary ionic strength adjuster and pH buffer. This method is considered easier and more reliable for making the necessary adjustments than the known addition procedure where these adjustments must be made in the sample before adding the known increment.

Potentiometric titration, the method used in our investigation, involves measuring and recording the potential difference (between two electrodes) as a titrant of precisely known concentration is added to a solution of the test element. At the beginning of the titration, the titrant is added in large increments; as the end point approaches, small increments are added. The end point or equivalent point is defined as the point at which the quantities of reacting species (the tested species and the titrant) are present in equivalent amounts. In a typical potentiometic titration, the titration is carried beyond the end point.

Sufficient time is allowed for the equilibrium to be reached after each titrant addition. A close approach to equilibrium is indicated when the measured potential difference (cell potential) stops to change or drift by more than a few millivolts. Good stirring is frequently effective in the titration process. Over most of the titration range the potential difference varies gradually, but near the end point it changes very abruptly. The titration curve is constructed by a plot of cell potential vs. the volume of titrant added, shown in Fig. 1. The equivalence point is defined as the midpoint in the steeply rising portion of the titration curve, where the maximum rate of change of cell potential per unit volume of added titrant exists. This approach for the determination of end point is referred to as a graphical approach. For other approaches, refer to reference (25).

Figure 1. Typical potentiometric titration curve.

Manual and Automatic Operation of Potentiometric Titration

For manual operation, the potential difference between the sulfide selective electrode and the double junction reference electrode was measured with a high input impedance pH/mV meter. [A voltmeter or pH/mV meter of 0.1 mV, 0.01 mV or better resolution can also be relied on for potential measurements.] The rest of

the equipment needed (which consists of simple volumetric glassware) is described in the following procedure. We observed that the analysis time of the potentiometric titration can be reduced considerably in black liquor by replacing the manual procedure with an automatic one through the use of automatic titrators. The automatic titrators enable the operator to perform other tasks while the instrument delivers the titrant in known increments, stops the delivery at a preselected end point, or continues beyond the end point. The titrators can also record the complete titration curve. From the curve, the end points are picked up and the concentration of tested species is calculated. In place of conventional burettes, the titrators are equipped with delivery units.

For routine analysis, a fully automatic unit is recommended. This unit will accept in series samples placed in a turntable. After each titration the turntable rotates, places the next sample solution beneath the electrode holder; lowers the electrode assembly, delivery tip, and stirring rod into the beaker; and activates the titration switch to perform the next titration. Each time, the syringe is refilled with titrant, and a printer prints out the amount of titrant delivered. This type of automatic instrument is ideal for performing multiple analyses in which the analytical procedure remains fixed over a period of time, as in a quality control situation.

Scope, Apparatus, Reagents, and Procedures of Potentiometric Titration

Manual Technique

Titrant - Mercuric Chloride ($HgCl_2$)

Scope

- This procedure describes the manual potentiometric method of sulfide analysis using mercuric chloride as titrant and double junction reference and silver-silver sulfide electrodes.

- From the plotting of titrant volume vs. corresponding millivolt readi s, the end point (vol. $HgCl_2$ to react with Na_2S in liquor) can be determined.
- This volume can then be used to calculate the concentration of Na_2S in the liquor sample. This procedure has been taken from NCASI Atmospheric Quality Improvement Technical Bulletin (34).

Apparatus

- pH meter with millivolt potential function
- Orion 90-00-02 double junction reference electrode, or equivalent
- Orion 94-16A silver/silver sulfide, sulfide-ion selective electrode, or equivalent
- 10-mL burette
- 250-mL beaker
- Magnetic stirrer with Teflon-covered magnetic stirring bar
- 5-mL transfer pipette
- 50-mL graduated cylinder

Reagents/Chemicals

- Analytical grade Na_2SO_3
- 4M NaOH
- 0.1000M $HgCl_2$

Procedure

- Add 3-5 g Na_2SO_3 to 250-mL beaker.
- Add 40 mL 4M NaOH to beaker.
- Dilute to approximately 120 mL with distilled water.
- Place beaker on magnetic stirrer. Stir to dissolve Na_2SO_3 crystals.
- Pipette 5 mL liquor into beaker; stir.
- Lower electrodes into sample.
- Turn function switch of pH meter from "Standby" to "mV."

- Record initial volume on burette and initial millivolt reading.
- Titrate with 0.1000M $HgCl_2$.
- Magnetic stirring is used continuously throughout the titration. The rate of stirring should not create a vortex or whip air into the solution.
- Record volume increments and corresponding millivolt readings for each volume increment addition.
- Millivolt readings should stabilize before adding the next volume increment of titrant.
- The end point region occurs when there is an abrupt and large change in potentials of 100 to 300 millivolts.

Data/Calculation

- Record volume increments and corresponding millivolt readings in columnar fashion.
- Plot data points on graph paper, with volume on the x-axis and millivolt readings on the y-axis.
- Draw a straight line with a ruler, connecting the points bordering the largest millivolt change. The resulting curve will be reversed S-shaped (see Fig. 1).
- Measure straight-line length. Divide the measurement by 2 and mark this point (volume end point) on the graph. Note this volume on the graph for calculation.
- Calculation

$$Na_2S \text{ g/L} = \frac{\frac{0.100M \ HgCl_2}{1000 \text{ mL}} \times \text{mL } HgCl_2 \times 78.04 \text{ g } Na_2S/\text{mole}}{0.005 \text{ L sample}}$$

Automatic Technique - Metrohm E636 Titroprocessor

Titrant - Cadmium Nitrate $Cd(NO_3)_2$

Scope

- This procedure describes sulfide analysis of kraft white liquor using the
- The E636 Titroprocessor automatically performs and plots a potentiometric sulfide analysis using 0.125M $Cd(NO_3)_2$ titrant.

Apparatus

- Metrohm E636 Titroprocessor
- Metrohm Dosimat E635 titrating stand
- Metrohm E649 magnetic stirrer
- Metrohm AG 9100 electrode
- 5-mL transfer pipette
- 25-mL graduated cylinder
- EA 1122/1 control card
- EA 1122/2 control card (calculation card optional)

Reagents*

- Sulfide antioxidant buffer, SAOB I
- 0.125M $Cd(NO_3)_2$

Instrument Parameters

- The instrument parameters are set by blackening the appropriate boxes on the EA 1122/1 control card.
- Control card markings

  Operation mode: Boxes 2 & 3

  Temp./°C: Darken applicable boxes for rows 1, 2, & 3

  Kinetics: Box 4

  Meas. Pt. Dens.: Box 3

*See Appendix for preparation of reagents.

Start V/mL: Row 1: Box 6
(for 20-mL burette)
Row 2: Box 0

Stop or EP, U/mV pH: Row 1: Box 0
Row 2: Box 5
Row 3: Box 3
Row 4: Box 0

Stop V/mL: Row 1: 9
(for 20-mL burette)
Row 2: 0

Stop EP No.: Leave all boxes blank

Scale U/mV, pH BEG: Row 1: Boxes 0 and 1
Row 2: Box 1

Scale U/mV, pH END: Row 1: Box 0
Row 2: Box 5

Procedure

- Preparation of sample
- Add 20 mL of distilled water to a 100-mL beaker.
- Add 20 mL of sulfide antioxidant buffer (SAOB I).
- Place a Teflon-covered magnetic stirrer bar into the beaker and place it on the E649 magnetic stirrer. Activate the magnetic stirrer and adjust the rate of stirring short of creating a vortex in the solution.
- Pipette 5 mL of liquor into the sample medium.
- Rinse the burette tip with distilled water over a waste beaker, then mount the burette tip into the sample medium.
- Initiate titration.
  - Feed the EA 1122/1 control card into the instrument. If a calculation method is to be programmed in conjunction with the titration, feed the EA 1122/2 card into the instrument also.
  - Initiate the titration according to the instruction manual.

- A titration curve is plotted during the sample run, with end point location identification. End point equivalent volume(s) are also listed. If a calculation method is used, the Na_2S concentration is also listed.

Data/Calculations

- Data
  - By using the "Report" key of the instrument, a report of parameter values set on and the titration conditions is given.
  - A complete list of all increment volumes and their corresponding potentials can be obtained by using the "Measuring Point List" function of the instrument.
- Calculation

$$Na_2S\ g/L = \frac{\frac{\text{Molarity } Cd(NO_3)_2}{1000} \times mL\ AgNO_3 \times 78.04\ g\ Na_2S/\text{mole}}{0.005\ L\ \text{sample}}$$

  - Automatic calculation may be obtained by utilization of the EA 1122/2 control card.

Titrant - Silver Nitrate ($AgNO_3$)

Scope

- This procedure describes sulfide analysis of kraft white liquor using the Metrohm E636 Titroprocessor equipped with a Dosimat E635 titrating stand and an E649 magnetic stirrer.
- The E636 Titroprocessor automatically performs and plots a potentiometric sulfide analysis using 0.2M $AgNO_3$ as titrant. This procedure is developed from TAPPI Standard T 625 ts-64 (3) for analysis of Na_2S in black liquors.

Apparatus

- Metrohm E636 Titroprocessor
- Metrohm Dosimat E635 titrating stand
- Metrohm E649 magnetic stirrer
- Metrohm AG 9100 electrode
- 5-mL transfer pipette and 10-mL measuring pipette
- 25-mL graduated cylinder
- EA 1122/1 control card
- EA 1122/2 control card (calculation card optional)

Reagents*

- 20% NaOH
- 1:99 ammonia
- 0.2M $AgNO_3$

Instrument Parameters

- The instrument parameters are set by blackening the appropriate boxes on the EA 1122/1 control card.
- Control card markings

  Operation mode: Boxes 2 & 3

  Temp./°C: Darken applicable boxes for rows 1, 2, & 3

  Kinetics: Box 4

  Meas. Pt. Dens.: Box 3

  Start V/mL: Row 1: Box 6 (for 20-mL burette)
  Row 2: Box 0

*See Appendix for preparation of reagents.

Stop or EP, U/mV pH: Row 1: Box 0

Row 2: Box 3

Row 3: Box 0

Row 4: Box 0

Stop V/mL: Row 1: Box 9 (for 20-mL burette)

Row 2: Box 9

Stop EP No.: Leave all boxes blank

Scale U/mV, pH BEG: Row 1: Boxes 0 and 1

Row 2: Box 1

Scale U/mV, pH END: Row 1: Box 0

Row 2: Box 2

Procedure

- Preparation of sample
  - Add 100 mL of distilled water to a 250-mL beaker.
  - Add 20 mL of 20% NaOH.
  - Pipette 7 mL of 1:99 ammonia into beaker.
  - Place a Teflon-covered magnetic stir bar into the beaker and place it on the E649 magnetic stirrer. Activate the magnetic stirrer and adjust the rate of stirring short of creating a vortex in the solution.
  - Pipette 5 mL of liquor into the sample medium.
- Rinse the burette tip with distilled water over a waste beaker, then mount the burette tip into the sample medium.
- Initiate titration
  - Feed the EA 1122/1 control card into the instrument. If a calculation method is to be programmed in conjunction with the titration, feed the EA 1122/2 control card into the instrument also.
  - Initiate the titration according to the instruction manual.

- A titration curve is plotted during the sample run, with end point location identification. End point equivalent volume(s) are listed. If a calculation method is used, the Na_2S concentration is also listed.

Data/Calculation

- Data
  - By using the "Report" key of the instrument, a report of parameter values set on and the titration conditions is listed. These may be supplemented by handwritten notes.
  - A complete list of all increment volumes and their corresponding potentials can be obtained by using the "Measuring Point List" function of the instrument.
- Calculation

$$Na_2S\ g/L = \frac{\frac{\text{Molarity } AgNO_3}{1000} \times \text{mL } AgNO_3 \times 39.025 \text{ g } Na_2S/\text{eq}}{0.005 \text{ L sample}}$$

  - Automatic calculation may be obtained by utilization of the EA 1122/2 control card.

Titrant - Mercuric Chloride ($HgCl_2$)

Scope

- This procedure describes sulfide analysis of kraft white liquor using the Metrohm E636 Titroprocessor equipped with a Dosimat E615 titrating stand and a E649 magnetic stirrer.
- The E636 automatically performs and plots a potentiometric sulfide analysis using 0.125M HgCl2 as titrant. This procedure is adopted from reference (34).

Apparatus

- Metrohm E636 Titroprocessor
- Metrohm Dosimat E635 titrating stand
- Metrohm E649 magnetic stirrer
- Metrohm AG 9100 electrode (silver billet with saturated KNO_3 internal reference upon which silver sulfide has been plated)
- 5-mL transfer pipette
- 50-mL graduated cylinder
- EA 1122/1 control card
- EA 1122/2 control card (calculation card optional)

Reagents/Chemicals

- 4M NaOH
- Na_2SO_3 crystals
- 0.125M $HgCl_2$

Instrument Parameters

- The instrument parameters are set by blackening the appropriate boxes on the EA 1122/1 control card.
- Control card parameters
  - Operator mode: Boxes 2 & 3
  - Temp./°C: Darken applicable boxes for rows 1, 2, & 3
  - Kinetics: Box 4
  - Meas. Pt. Dens.: Box 3
  - Start V/mL: Row 1: Box 6 (for 20-mL burette)
    Row 2: Box 0
  - Stop or EP, U/mV pH: Row 1: Box 0
    Row 2: Box 3
    Row 3: Box 0
    Row 4: Box 0

- Stop V/mL: Row 1: Box 9
  (for 20-mL burette)
  Row 2: Box 0
- Stop EP No.: Leave all boxes blank
- Scale U/mV, pH BEG: Row 1: Boxes 0 and 1
  Row 2: Box 1
- Scale U/mV, pH END: Row 1: Box 1
  Row 2: Box 2

Procedure

- Preparation of sample
  - Add 40 mL 4M NaOH to a 250-mL beaker. Place beaker on E649 magnetic stirrer. Place a Teflon-covered magnetic stir bar in the beaker and activate the magnetic stirrer.
  - Add 5 g Na_2SO_3 crystals.
  - Add 60 mL of distilled water.
  - Continue stirring until the Na_2SO_3 crystals are dissolved.
  - Adjust the rate of stirring short of creating a vortex in the solution.
  - Pipette 5 mL of liquor into the sample medium.
  - Rinse the burette tip with distilled water over a waste beaker, then mount the burette tip into the sample medium.
- Initiate Titration
  - Feed the EA 1122/1 control card into the instrument. If a calculation method is to be programmed in conjunction with the titration, feed the EA 1122/2 control card into the instrument also.
  - Initiate the titration according to the instruction manual.
  - A titration curve is plotted during the sample run, with end point(s) location(s). End point(s) equivalent volume(s) are listed. If a calculation method is also used, the Na_2S concentration is also listed.

Data/Calculation

- Data
  - By using the "Report" key of the instrument, a report of parameter values set on and the titration conditions is listed. These may be supplemented by handwritten notes.
  - A complete list of all increment volumes and their corresponding potentials can be obtained by using the "Measuring Point List" function of the instrument.
- Calculation

$$Na_2S\ g/L = \frac{\frac{0.125M\ HgCl_2}{1000} \times mL\ HgCL_2 \times 78.04\ g\ Na_2S}{0.005\ L\ sample}$$

  - Automatic calculation may be obtained by utilization of the EA 1122/2 control card.

Automatic Technique - Mettler DL40 MemoTitrator

Titrant - Silver Nitrate ($AgNO_3$)

Scope

- This procedure describes sulfide analysis of kraft white liquor using the Mettler DL40 MemoTitrator (36) and 0.1000M $AgNO_3$ as titrant [see reference (3)].

Apparatus

- Mettler DL40 MemoTitrator
- Mettler GA 40 Printer
- Orion 90-00-02 double junction reference electrode, or equivalent.
- Orion 94-16A silver/silver sulfide, sulfide-ion selective electrode, or equivalent.

- 5-mL and 10-mL transfer pipettes
- (2) 25-mL graduated cylinders

Reagents*

- 20% NaOH
- 1:99 ammonia
- 0.1000M $AgNO_3$

Instrument Parameters

- The titration parameters must be entered into the automatic titrator by the operator.

Parameters

- Method No.: Selected by operator
- Method: End point relative
- Reagent No.: Selected by operator
- Link to method: 0 (or to programmed calculation method)
- Input code: 1000
- Result unit: -5
- Constant: 1
- Max. volume mL: 90
- Stir time S: 3
- mV or PX 0/1: 0
- Trend 1/-1: 1
- End point relative: 454
- Control band: 471
- Delay S: 5

*See Appendix I for preparation of reagents.

Procedure

- Set up the burette according to the instruction manual.
- Sample preparation
  - Add 25 mL of 20% NaOH to sample cup.
  - Add 10 mL of 1:99 ammonia.
  - Add 15 mL of distilled water.
  - Pipette 5 mL of liquor into sample cup.
  - Rinse burette tip into a waste beaker using the "Rinse Tip" function of the instrument. Mount burette tip into sample cup.
  - Initiate titration according to the instruction manual using 0.1000M $AgNO_3$ as titrant and electrodes noted in Section 2.

Data/Calculations

- Resultant equivalent volume is automatically recorded on the GA 40 Printer.
- Calculation

$$Na_2S\ g/L = \frac{\frac{0.1000M\ AgNO_3}{1000\ mL} \times mL\ AgNO_3 \times 39034\ g\ Na_2S/eq}{0.005\ L\ sample}$$

- A calculation method based upon equation in 6.2.1 may also be programmed into the computer.

Titrant - Mercuric Chloride ($HgCl_2$)

Scope

- The Mettler mercuric chloride potentiometric titration is an adaptation of the manual mercuric chloride titration (34) to the Mettler DL40 MemoTitrator.

Apparatus

- Mettler DL40 MemoTitrator
- Mettler GA 40 Printer
- 5-mL transfer pipette

- 25-mL graduated cylinder
- Orion 90-00-02 double junction reference electrode, or equivalent.
- Orion 94-16A silver/silver sulfide, sulfide ion selective electrode, or equivalent.

Reagents*

- Analytical grade Na_2SO_3
- 4M NaOH
- 0.1000M $HgCl_2$

Instrument Parameters

- The titration parameters must be entered into the automatic titrator by the operator.
- Parameters
  - Method No: Selected by operator
  - Method: End point relative
  - Reagent No.: Selected by operator
  - Link to method: 0 (or to programmed calculation method)
  - Input code: 1000
  - Result unit: -5
  - Constant: 1
  - Max. volume mL: 45
  - Stir time S: 3
  - mV or PX 0/1: 0
  - Trend 1/-1: 1
  - End point relative: 410
  - Control band: 369
  - Delay S: 5

*See Appendix I for preparation of reagents.

Procedure

- Set up the burette according to the instruction manual.
- Sample preparation
- Add 40 mL 4M NaOH to sample cup.
- Add 3-5 g Na_2SO_3 crystals; stir.
- Add 15 mL distilled water; stir.
- Pipette 5 mL of liquor sample into sample cup.
- Rinse burette tip into a waste beaker using the "Rinse Tip" function of the instrument. Mount burette tip into sample cup.
- Initiate titration according to the instruction manual. Titration is automatically carried out to completion.

Data/Calculation

- Resultant equivalent volume is automatically recorded on the GA 40 Printer.

  Data

$$Na_2S\ g/L = \frac{\frac{0.1000M\ HgCl_2}{1000\ mL} \times mL\ HgCl_2 \times 78.04\ g/mole}{0.005\ L\ sample}$$

  - A calculation method may be programmed into the titrator.

POLAROGRAPHIC METHODS

Introduction and Principles

The development and introduction of polarography by Heyrovsky in 1922 (37) marked a significant advance in electrochemical methodology. In polarography, the element of selectivity was introduced by the control of electrode potential. This element of selectivity was missing in the older electrochemical methods of conductometry and potentiometry. Polarography is an attractive electrochemical technique, because it is versatile, rapid, sensitive, and accurate (38). One of its great advantages is that only a small volume (in the μL range) is needed for analysis.

Because a minute amount of the sample is consumed, the analysis can be repeated several times on the same sample. Another advantage of the method is that several species can be determined in sequence from a single test.

In this section, we introduce some of the important parameters we considered necessary for the understanding of the principle of polarography. For further information, see references (39-46).

Polarographic Cell

The polarographic method is based on the current-voltage curves arising at a microelectrode when diffusion is the rate-determining step in the electrochemical reaction.

Conventional polarography uses a small polarizable microelectrode and a layer of mercury as the counter and reference electrode. In new models of polarographic analyzers, the cell is composed of the microelectrode, a platinum wire as the counter electrode, and an Ag/AgCl or saturated calomel electrode (SCE) as the reference electrode. The reference electrode is of constant potential, is positioned as close as possible to the mercury drop, and can sense the potential at that point. It is connected to the polarograph through a circuit that draws essentially no current.

The most commonly used type of microelectrode is the dropping mercury electrode (DME). It is produced by passing a stream of mercury through a very fine capillary to provide a continuous steady flow of identical droplets. The dropping mercury electrode has the following advantages: (1) its surface is reproducible, (2) constant removal of the electrode surface eliminates passivity or poisoning effects, (3) the high overpotential of hydrogen permits polarographic reduction of electroactive species, (4) mercury forms amalgams with many metals and thereby lowers their reduction potential, and (5) reproducible average currents are instantly achieved.

Polarogram (current-voltage curve)

The current-voltage curves arising at the microelectrode are called polarograms. Two parameters are of interest in the current-voltage curves: the half-wave potential and the limiting diffusion current. The half-wave potential is the potential at the point of inflection of the current-voltage curve, one half the distance between the residual current* and the limiting diffusion current** (i_d) plateau (see Fig. 2), i.e., when $i = \frac{id}{2}$, $E = E_{1/2}$. The half-wave potential is a characteristic of the electroactive species in a given medium. It is also independent of the concentration of the reacting species if the electrochemical reaction of the reacting species is rapid and reversible. The half-wave potential provides qualitative information about the chemical composition of the solution to be analyzed.

Quantitative information from polarographic analysis is based on the direct proportionality between diffusion current and concentration of the reactive species in the bulk of the solution. The fundamental equation developed by D. Ilkovic in 1934 (47) relating the concentration and other parameters to the diffusion current is

$$i_d = .607\ n\ D^{1/2}\ m^{2/3}\ t^{1/6}\ C$$

where i_d is the average diffusion current in microamperes during the lifetime of a drop. The quantity n is the number of equivalents per mole of the electrode reaction; D is the diffusion coefficient for the reactive species expressed in cm^2/sec; m is the rate of mercury flow in mg/sec; t is the drop/time in sec; and C is the concentration of the reactant in mmoles/L. The product $m^{2/3}\ t^{1/6}$ in the equation is called the capillary constant. This equation is called the Ilkovic equation.

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* Residual current may originate from the reduction of impurities present in the blank solution.

** Diffusion current results when the electrochemical reaction at the electrode surface is controlled by the diffusion of reactive species from the bulk solution to the electrode/solution interface. Limiting diffusion current is the maximum diffusion rate by which reactive species are brought to the electrode solution interface.

Figure. 2. Important parameters on a typical polarogram by conventional polarography.

A reacting species in an electrolytic solution may be transported to an electrode surface by three mass-transfer processes: 1) diffusion under the influence of the concentration gradient, 2) migration of charged ions in an electric field, and 3) convection due to motion of the solution or the electrode. In polarography every effort is made to eliminate the convection and migration contributions by not stirring the solution and by using a large excess of nonreactive supporting electrolyte, respectively. The role of the ions of the supporting electrolyte is to ensure that the reactive species are mainly transported to the surface by diffusion effect

and not by electrostatic effect. It is generally advised that the supporting electrolyte concentration be 50 to 100 times greater than the concentration of the reactive species to eliminate migration currents. The supporting electrolyte in our investigation was NaOH for the sulfide determination and acetate solution for the sulfite and thiosulfate. Besides acting as supporting electrolytes, NaOH and acetate provide the proper pH media for analysis of sulfide (pH = 14) and sulfite and thiosulfate (pH = 4.5).

Current-time Response

When a linearly varying dc potential is applied between the microelectrode and the reference electrode, a current is recorded between the microelectrode and the counter electrode. There are two major components to the current - the charging current and the faradaic current (Fig. 3). The charging current is the current required to charge the electrode double layer. The faradaic current is proportional to the concentration of the reactive species, and in polarographic analysis is equal to the diffusion current.

The charging current is considered the principal factor limiting the sensitivity of polarography and its accuracy at low concentrations. At concentrations of reactive species of 10^{-3}M or greater, the charging current is negligible compared with the faradaic current and may be ignored. At concentrations of 10^{-4}M, the charging current is an appreciable fraction of the total current, and a correction must be made for it. At concentrations around 10^{-5}M, the charging current is usually larger than the faradaic current. The precision of the polarographic analysis depends principally on how precisely the contribution of the charging current can be estimated and compensated.

The charging current may be minimized when 1) the change of potential is slow enough to be negligible during a drop period, and 2) the current measurement is made near the end of a drop life, where the area is changing slowly. As shown in

Fig. (3), the faradaic current is greatest in the short time interval just prior to the drop fall. A very productive approach to minimize the charging current and to increase the faradaic current contribution is to permit current measurements to be taken during a short period near the end of the drop life. This can be accomplished by a timing or gating system.

Figure 3. Faradaic and charging currents as a function of time.

Despite the timing system in the conventional dropping mercury electrode (DME), the charging current is not completely eliminated due to the continuous

growth of the drop. However, in the newly developed static mercury electrode (SMDE), the drop is allowed to grow until it reaches the desired size. Once the desired size is reached, the mercury flow is stopped and the drop area remains constant until the drop is dislodged. Therefore with the SMDE, the final current does not contain the drop growth-induced charging component characteristic of the DME.

Oxygen Interference and the Importance of Deaeration (48)

Three significant complications can arise if oxygen is not removed from the solution to be analyzed.

1. Reaction between oxygen and metallic mercury

$$O_2 + 2Hg + 2Cl + 2\ H_2O \rightarrow H_2O_2 + Hg_2Cl_2 + 2OH^-$$

2. Hydrogen peroxide formation which can act as both oxidizing and reducing agent; H_2O_2 is formed as a result of the first stage of electrochemical reduction of O_2 in acid, neutral, and alkaline media as follows:

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2 \text{ (acid media)}$$

$$O_2 + 2H_2O + 2e \rightarrow H_2O_2 + 2OH^- \text{ (neutral and alkaline media)}$$

$$E_{1/2} \cong 0.05V \text{ vs. SCE}$$

3. Increase in pH in the vicinity of the mercury electrode. This results from the second-stage electrochemical reduction of O_2 in acid, neutral, and alkaline media as follows:

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \text{ (acid media)}$$

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \text{ (neutral or alkaline media)}$$

$$E_{1/2} = -0.5V \text{ to } -1.3V \text{ vs. SCE.}$$

To eliminate the interference of oxygen, deaeration is performed prior to the polarographic analysis. There are several ways to remove oxygen from the solution:

1. Addition of sodium sulfite
2. Purging with prepurified nitrogen

Due to expected interference in sulfite determination and to possible interaction of the added sulfite with sulfide and thiosulfate, we refrained from using sulfite as the deoxygenating agent.

Prepurified nitrogen was used in our analytical investigation because 1) the technique of its nitrogen purge is convenient and 2) no interference is expected from the presence of nitrogen.

Since prepurified nitrogen direct from the tank contains a few parts per million of oxygen, an oxygen-scrubbing system was used to remove the traces of oxygen. Oxygen-scrubbing systems in general include passage of a nitrogen stream through 1) a quartz tube containing copper turnings heated to 450-550°C (48), 2) vanadous chloride solution* (48), 3) a catalyst containing 30% copper highly dispersed on a carrier with activating substances in the form of pellets (48), and 4) a prepackaged cylinder of a chromic oxide (48). In our investigation, vanadous* chloride was used to assure the use of nitrogen oxygen free gas.

Concentration Determination

As previously discussed, the concentration of the reactive species may be determined from the direct proportionality between diffusion current density and the concentration of the species. Residual currents, which may originate from the reduction of trace impurities present in the blank solution and from the charging current resulting from the mercury-solution interface, interfere with obtaining a

[a]See Appendix for preparation of vanadous chloride.

direct proportionality between diffusion current and the concentration. To eliminate or minimize the residual current, the polarographic behavior of a blank solution is determined. The blank solution in our investigation was composed of the supporting electrolyte, NaOH, and acetate buffer used for the polarographic analysis of sulfide, and sulfite and thiosulfate, respectively.

To establish the range of direct proportionality between limiting diffusion current and concentration of the reactive species, a series of standard solutions (i.e., of known concentration) is used. The standard solutions should be as identical as possible to the samples to be analyzed. They should also cover a concentration range within which the unknown sample will likely fall. The concentration of the standards will then be plotted vs. the limiting diffusion current determined from polarographic analysis. From such a plot, the linearity of the current concentration relationship can be assessed. If the curve is not linear, a curve can be constructed that will allow analysis. Figures 4-6 present the current-concentration plot for Na_2S, $Na_2S_2O_3$, and Na_2SO_3.

In general, these plots are referred to as standard curves. The Model 384 polarographic analyzer can perform the standard curve function automatically. If this function is not available in a polarographic analyzer, standard curves can be constructed normally like the ones shown in Fig. 4-6.

The function for automatic determination of standard curves is limited to a series of three standard solutions. If desired, however, a series of these 3-point standards can be stored within the instrument, with each 3-point standard bracketing a specific concentration range.

Figure 4. Linearity study of Na_2S at 10^{-7} to 10^{-4} M by differential pulse polarography.

Figure 5. Linearity study for $Na_2S_2O_3$ at 10^{-7} to 19^{-6}M (upper curve) and at 10-5 to 10-2M (lower curve) by differential pulse polarography.

Figure 6. Linearity study for Na_2SO_3 at 10^{-7} to 10^{-4}M (upper curve) and at 10-5 to 10-2M (lower curve) by differential pulse polarography.

This method of sample analysis is called the "standard curve" and is utilized as follows. First, three standard solutions of the species of interest are prepared, each consisting of a different concentration. Each standard is then analyzed separately, with the peak potential, peak current, and the peak concentration being entered into the data files of the instrument through a secondary playback of the polarogram. Once the standard information has been processed and stored, the linearity of the current-concentration relationship can be automatically determined (graphed) by utilizing the "Function 4" button of the instrument.

Subsequent sample analyses can be performed quite simply by running a blank, loading the sample, selecting the "standard curve" method of calculation, and then running the sample. The peak current, peak concentration, and peak potential information is automatically listed on the resulting polarogram of the sample.

Another useful technique is the standard addition method. The polarogram of an exactly known volume of the sample solution is obtained. Then a carefully measured quantity of a standard solution of the substance of interest is added and the polarogram is again obtained. From the increase in wave height and the quantity of standard added, the concentration of the original solution can be calculated (see following page). The analyst must assume, however, that the concentration-current relationship is linear (see Fig. 4-6). This procedure is particularly effective when the diffusion current is sensitive to other components of the solution introduced with the sample.

The standard addition method of concentration determination can be performed automatically on the Model 384 Polarographic Analyzer in the following manner: first, a standard solution containing the species of interest is prepared so that the species concentration lies within a known linearity range. A blank is then run on the polarographic medium. The sample of known volume is then loaded and run.

A polarogram of the unknown sample concentration is plotted following the sample run. The peak current and peak potential values are listed on this polarogram, but the sample concentration is still unknown. The sample is then "spiked" with a standard of known volume and concentration. A standard run is then performed in much the same manner as the sample run. A playback of the standard then follows with a listing of the standard peak current and peak potential values. The operator must then enter the known concentration of the standard and initiate a secondary playback of the standard. The secondary playback is identical to the first playback, with the exception that the standard concentration is now "known" and listed, and the peak current, peak potential, and peak concentration values have been entered into the standard-data files of the instrument. The concentration of the sample can now be obtained by initiating a secondary playback of the sample using the standard addition calculation function.

The difference in the computation process between standard curve and standard addition is directly related to procedural differences. It is therefore necessary that the instrument be "informed" by the operator of the standards method selected. In the standard curve method, the concentration is computed by comparing the peak height of the sample to the peak height of the known standard concentration. In the standard addition method, the concentration is computed by comparing the playback peak height before spiking with the peak height plotted after spiking. If it were necessary to do so, the same result using the standard addition method could be obtained by hand calculation using the equation:

$$C_u = \frac{C_s \; Xi_s \; X \; v_s}{(i_t - i_s) \; x \; v_u}$$

where

C_u = concentration of unknown in sample

C_s = concentration of standard

i_t = peak current of sample plus standard

i_s = peak current of sample

v_s = volume of standard added (μL)

v_s = volume of sample (μL)

Scope, Apparatus, Reagents, and Procedures - Differential Pulse Polarographic Method

Sulfide Analysis

Scope

- This procedure describes a method of sodium sulfide analysis in kraft white or weak black liquor using a PAR Model 384 Polarographic Analyzer (49). It is adopted from the procedures described by Noel (5) and Renard et al. (23).
- Analyses are conducted using the Differential Pulse Mode of the instrument, with standard addition as the concentration calculation method.
- Oxygen is removed from the system by purging the polarographic medium with oxygen-free nitrogen that has passed through an oxygen-scrubbing tower. Nitrogen from the tank first passes through a gas scrubbing tower filled with vanadous chloride solution containing zinc amalgam at the bottom of the tower. Before entering the sample medium, nitrogen passes through a second tower filled with 0.2M NaOH solution, identical to the polarographic medium.

Apparatus

- PAR Model 384 Polarographic Analyzer
- PAR Model 303 Static Mercury Drop Electrode
- (2) Pyrex gas scrubbing towers

- Gilson PIPETMAN adjustable digital microliter pipette, or equivalent
- Houston Hi-Plot Digital Plotter, or equivalent x-y recorder.
- (4) 100-mL volumetric flasks
- (3) 10-mL and (2) 50-mL transfer pipettes

Solutions

- 0.2M NaOH (Polarographic Medium)
- SAOB I
- 50 g/L Na_2S: Prepare by dissolving 15.4 g $Na_2S \cdot 9H_2O$ crystals that have been thoroughly rinsed with distilled water and blotted dry in 50 mL SAOB I. Transfer to 100-mL volumetric flask. Dilute to mark with distilled water. Standardize potentiometrically against 0.1M $Cd(NO_3)_2$ using Orion 94-16A and 90-00-02 electrodes.

Preparation of Na_2S Polarographic Standard

- Pipette 10 mL of 50 g/L Na_2S stock solution obtained in Section 3.3 into a 100-mL volumetric flask containing 50 mL of SAOB I. Dilute to mark with distilled water and mix thoroughly.
- Dilute a second time by pipetting 10 mL of 5 g/L Na_2S obtained above into a second 100-mL volumetric flask containing 50 mL of SAOB I. Dilute to mark with distilled water.

Preparation of Sample

- Pipette 10 mL of liquor into a 100-mL volumetric flask containing 50 mL SAOB I. Dilute to mark with distilled water and mix well.
- Pipette 10 mL of diluted liquor obtained above into a second 100-mL volumetric flask containing 50 mL of SAOB I. (Note: The dilutions of the standard and sample have been deliberately made identical so that dilution factors need not be considered when entering the standard concentration into the Standard Data

File of the instrument. Thus, the PPB or PPM result concentration registered by the instrument following analysis can be directly read as g/L Na_2S).

DPP Parameters

- Technique selection: Differential Pulse Polarography

Run Parameter Keys

- Initial potential: -900 millivolts
- Final potential: -400 millvolts
- Pulse height: 25 millivolts
- Sample number: Entered for each sample run
- Purge time: Blank: 240 sec
  Sample: 420 sec
  Standard: 180 sec
- Date: Day, month, and year sample is analyzed
- Scan Rate: 4 mV/sec (Set by "Drop Time" and "Scan Increment" keys)
- Drop time: 1.0 sec
- Scan Increment: 4 mV
- Other keys: Do not apply for DPP

Playback and Calculation Parameter Keys

- Standard addition
- Peak potential: Value entered after initial playback of standard run
- Peak concentration: Value entered after initial playback of standard run
- Clear standard data: Key depressed prior to next sample analyses followed by depressing the "Yes" key.
- Override: 10 auto playback: Yes
  11 plot run data: No
  12 plot playback data: Yes
  13 plot results: Yes

14 RS 232 playback data: No

15 RS 232 results: No

16 real-time data smoothing: Yes

17 invert playback data: No

- Tangent fit: Yes
- Blank subtract: Yes
- Peak location: Yes
- Other keys: Not used

Procedure

- Set all DPP parameters according to run parameter keys, page __.
- Pipette 10 mL 0.2M NaOH into sample cup and mount onto Model 303 SMDE.
- Depress "Purge Time" key and enter 240 on the numerical keys.
- Blank run.
- Press the "Blank" key.
- Press the "Run" key.
- The polarographic medium is automatically purged with oxygen-free nitrogen for 240 sec, and a curve is automatically plotted on the recorder following the blank run.
- Sample run
  - Pipette 50 mL of sample into the sample cup using the microliter pipette
  - Press the "Purge Time" key and enter a value of 420 using the numerical keys.
  - Press the "Sample" and "Run" keys.
  - The sample is automatically purged for 420 sec prior to analysis. Upon completion of the sample run, a sample curve is automatically

plotted with the blank being subtracted. The peak potential and peak current values are also recorded.

- Standard run.
- Pipette 50 µL of standard Na_2S into the sample cup with a microliter pipette.
- Press the "Purge Time" key and enter a value of 180 using the numerical keys.
- Press the "Standard" and "Run" keys. The Standard (including sample) run is initiated following a purge of 180 seconds. Upon completion of the run, the curve is automatically played back with a listing of the peak potential and peak current values.
- Press the "Peak Potential" key and enter the peak potential listed on the standard playback.
- Press the "Peak Concentration" key and enter the known concentration of the Na_2S standard in either PPB or PPM. (Enter the actual g/L concentration, i.e., before dilution, as PPB or PPM. Conversion to actual PPB or PPM is not necessary. This enables the PPB or PPM result concentration to be read directly as g/L.)
- Press the "Standard" and "Playback" keys. The standard curve is played back a second time, including a listing of the peak potential, peak current, and peak concentration. The second playback of the standard allows the standard concentration to be set up in the standard data files of the instrument.

• Sample playback

- Press the "Sample" and "Playback" keys. The sample curve is played back a second time, with a listing of the sample peak potential, peak current,

and peak concentration. The peak concentration (PPB or PPM) can be read directly as g/L.

Thiosulfate Analysis

Scope

- This procedure describes a method of sodium thiosulfate analysis in kraft white or weak black liquors using a PAR Model 384 Polarographic Analyzer.
- Analyses are conducted using the Differential Pulse Mode of the instrument, with standard addition as the concentration calculation method.
- Oxygen is removed from the system by purging the polarographic medium with oxygen-free nitrogen that has been passed through an oxygen-scrubbing tower. Nitrogen from the tank first passes through a gas scrubbing tower filled with vanadous chloride solution containing zinc amalgam at the bottom of the tower. Before entering the sample medium, nitrogen passes through a second tower filled with 0.5M acetate buffer, identical to the polarographic medium.

Apparatus

- PAR Model 384 Polarographic Analyzer
- PAR Model 303 Static Mercury Drop Electrode
- (2) Pyrex gas scrubbing towers
- Gilson PIPETMAN adjustable digital microliter pipette, or equivalent
- Houston Hi-Plot Digital Plotter, or equivalent x-y recorder
- (2) 100-mL volumetric flasks
- (3) 10-mL transfer pipettes

Solutions

- 0.5M acetate buffer
- 0.1M $Na_2S_2O_3$ standard (standardized against 0.2M iodine)

Preparation of $Na_2S_2O_3$ Polarographic Standard

- Pipette 10 mL of 0.1M $Na_2S_2O_3$ standard into a 100-mL volumetric flask.
- Dilute to mark with distilled water. Mix well.
- $Na_2S_2O_3$ g/L = Molarity $Na_2S_2O_3$ x 158.1

  (Dilution factor does not need to be considered, as the sample will have the same dilution factor.)

Preparation of Sample

- Pipette 10 mL of liquor into a 100-mL volumetric flask.
- Dilute to mark with distilled water.

  (Note: The dilutions of the standard and sample have been deliberately made identical so that dilution factors need not be considered when entering the standard concentration into the Standard Data File of the instrument. Thus, the PPB or PPM result concentration of the sample calculated by the instrument following analysis can be directly read as g/L $Na_2S_2O_3$.)

DPP Parameters

- Technique Selection: Differential pulse polarography
- Run Parameter Keys
  - Initial Potential: -0.400V
  - Final Potential: 0.000V
  - Pulse Height: 0.25V
  - Sample Number: Entered for each sample run
  - Purge Time: Blank: 240 sec
    Sample: 420 sec
    Standard: 180 sec
  - Date: Day, month, and year sample is analyzed
  - Scan Rate: 4 mV/sec (set by "DROP TIME" and "SCAN INCREMENT" keys)
  - Drop Time: 1.0 sec

- Scan Increment: 4 mV

-Other Keys: Do not apply for DPP

• Playback and Calculation Parameter Keys

- Standard Addition
- Peak Potential: Value entered after initial playback of standard run
- Peak Concentration: Value entered after initial playback of standard run
- Clear Standard Data: Key depressed prior to next sample analysis followed by depressing the "Yes" key
- Override: 10 Autoplayback: Yes
  11 Plot Run Data: No
  12 Plot Playback Data: Yes
  13 Plot Results: Yes
  14 RS 232 Playback Data: No
  15 RS 232 Results: No
  16 Real-time Data Smoothing: Yes
  17 Invert Playback Data: No
- Tangent Fit: Yes
- Blank Subtract: Yes
- Peak Location: Yes
- Other Keys: Not used

Procedure

• Set all DPP parameters according to Run Parameters Keys, page, __.

• Pipette 10 mL of 0.5M acetate buffer into sample cup and mount onto Model 303 SMDE.

• Blank run.

• Press "Purge Time" key and enter 240 using the numerical keys.

• Press the "Blank" key.

- Press the "Run" key.
- The polarographic medium is automatically purged with oxygen-free nitrogen for 240 sec, and a curve is automatically plotted on the recorder following the blank run.
- Sample run.
- Pipette 50 µL of sample into the sample cup using the microliter pipette.
- Press the "Purge Time" key and enter a value of 420 with the numerical keys.
- Press the "Sample" and "Run" keys.
- The sample is automatically purged for 420 sec prior to analysis. Upon completion of the sample run, a sample curve is automatically plotted with the blank being subtracted. The peak potential and peak current values are also recorded.
- Standard run
  - Pipette 50 µL of $Na_2S_2O_3$ standard into the sample cup by using a microliter pipette.
  - Press the "Purge Time" key and enter a value of 180 with the numerical keys.
  - Press the "Standard" and "Run" keys. The Standard (including sample) Run is initiated following a purge of 180 sec. Upon completion of the run, the standard curve is automatically played back with a listing of the peak potential and peak current values.
  - Press the "Peak Potential" key and enter the peak potential listed on the standard playback.
  - Press the "Peak Concentration" key and enter the known concentration of the $Na_2S_2O_3$ standard in either PPB or PPM. (Enter the actual g/L concentration of the 0.1M $Na_2S_2O_3$ standard before dilution as PPB or PPM.

This enables the PPB or PPM result concentration of the sample to be read directly as g/L.)

- Press the "Standard" and the "Playback" keys. The standard curve is played back a second time, including a listing of the peak potential, peak current, and peak concentration. The second playback of the standard allows the standard concentration to be set up in the standard data files of the instrument.

• Sample Playback

- Press the "Sample" and "Playback" keys. The sample curve is played back a second time, with a listing of the sample peak potential, peak current, and peak concentration. The peak concentration (PPB or PPM) can be read directly as g/L.

Sulfite Analysis

Scope

- This procedure describes a method of sodium sulfite analysis in kraft white or weak black liquors using a PAR Model 384 Polarographic Analyzer.
- Analyses are conducted using the differential pulse mode of the instrument, with standard addition as the concentration calculation method.
- Oxygen is removed from the system by purging the polarographic medium with oxygen-free nitrogen that has been passed through an oxygen-scrubbing tower. Nitrogen from the tank first passes through a gas scrubbing tower filled with vanadous chloride solution containing zinc amalgam at the bottom of the tower*. Before entering the sample medium, nitrogen passes through a second tower filled with 0.5M acetate buffer, identical to the polarographic medium.

*See Appendix I for preparation of the oxygen scrubbing solution.

Apparatus

- PAR Model 384 Polarographic Analyzer
- PAR Model 303 Static Mercury Drop Electrode
- (2) Pyrex gas scrubbing towers
- Gilson PIPETMAN adjustable digital microliter pipette, or equivalent
- Houston Hi-Plot Digital Plotter, or equivalent x-y recorder
- (2) 100-mL volumetric flasks
- (2) 10-mL transfer pipettes

Solutions

- 0.5M acetate buffer
- 0.2M Na_2SO_3 stock solution
- Acetate buffer for Na_2SO_3 Polarographic Standards

Preparation of Na_2SO_3 Polarographic Standard

- Pipette 10 mL of acetate buffer (for Na_2SO_3 standards) into a 100-mL volumetric flask.
- Pipette 5 mL of standardized 0.2M Na_2SO_3 stock solution into the flask.
- Dilute to mark with distilled water and mix well.
- Na_2SO_3 g/L = $\frac{\text{Molarity } Na_2SO_3}{2} \times 126.0$

  (The denominator of 2 stems from the difference in dilution between the standard and the sample.)

Preparation of Sample

- Pipette 10 mL of acetate buffer for sulfite solutions into a 100-mL volumetric flask.
- Pipette 10 mL of liquor into the flask.
- Dilute to mark with distilled water and mix well.

DPP Parameters

- Technique Selection: Differential pulse polarography

- Run Parameter Keys
  - Initial Potential: -0.900V
  - Final Potential: -0.452V
  - Pulse Height: 0.025V
  - Sample Number: Entered for each sample run
  - Purge Time: Blank: 240 sec
    Sample: 420 sec
    Standard: 180 sec
  - Date: Day, month, and year sample is analyzed.
  - Scan Rate: 4 mV/sec (set by "DROP TIME" and "SCAN INCREMENT" keys)
  - Drop Time: 1.0 sec
  - Scan Increment: 4 mV
  - Other Keys: Do not apply for DPP.
- Playback and Calculation Parameter Keys
  - Standard addition
  - Peak Potential: Value entered after initial playback of standard run
- Peak Concentration: Value entered after initial playback of standard run
- Clear Standard Data: Key depressed prior to next sample analysis followed by depressing the "Yes" key.
- Override: 10 Autoplayback: Yes
  11 Plot Run Data: No
  12 Plot Playback Data: Yes
  13 Plot Results: Yes
  14 RS 232 Playback Data: No
  15 RS 232 Results: No
  16 Realtime Data Smoothing: Yes
  17 Invert Playback Data: No

- Tangent Fit: Yes
- Blank Subtract: Yes
- Peak Location: Yes
- Other Keys: Not used

Procedure

- Set all DPP parameters according to Run Parameter Keys.
- Pipette 10 mL of 0.5M acetate buffer into sample cup and mount onto Model 303 SMDE.
- Blank run
  - Press "Purge Time" key and enter 240 with the numerical keys.
  - Press the "Blank" key.
  - Press the "Run" key.
  - The polarographic medium is automatically purged with oxygen-free nitrogen for 240 sec, and a curve is automatically plotted on the recorder following the blank run.
- Sample run
  - Pipette 50 µL of sample into the sample cup using the microliter pipette.
  - Press the "Purge Time" key and enter a value of 420 with the numerical keys.
  - Press the "Sample" and "Run" keys.
  - The sample is automatically purged for 420 sec. Upon completion of the sample run, a sample curve is automatically plotted with the blank being subtracted. The peak potential and peak current values are also recorded.
- Standard run
  - Pipette 50 µL of Na_2SO_3 standard into the sample cup using a microliter pipette.

- Press the "Purge Time" key and enter a value of 180 with the numerical keys.
- Press the "Standard" and "Run" keys. The Standard (including sample) Run is initiated following a purge of 180 sec. Upon completion of the run, the standard curve is automatically played back with a listing of the peak potential and peak current values.
- Press the "Peak Potential" key and enter the peak potential listed on the standard playback.
- Press the "Peak Concentration" key and enter the known concentration of the Na_2SO_3 standard in either PPB or PPM. (Enter the actual concentration of the $\frac{Na_2SO_3 \text{ before dilution}}{2}$. This enables the PPB or PPM result concentration of the sample to be read directly as g/L.)
- Press the "Standard" and the "Playback" keys. The standard curve is played back a second time, including a listing of the peak potential, peak current, and peak concentration. The second playback of the standard allows the standard concentration to be set up in the standard data files of the instrument.

• Sample Playback

- Press the "Sample" and "Playback" keys. The sample curve is played back a second time, with a listing of the sample peak potential, peak current, and peak concentration. The peak concentration (PPB or PPM) can be read directly as g/L.

ABC METHOD

Introduction and Principles

The ABC method (4) is a volumetric method used widely in the paper industry for the determination of effective alkali (NaOH + 1/2 Na_2S), active alkali (NaOH + Na_2S), and total alkali (NaOH + Na_2S + Na_2CO_3).

It consists of three distinct and continuous steps. In the A step, the effective alkali (NaOH + 1/2 Na_2S) of the liquor is determined. A standard solution of hydrochloric acid is used as the titrant, and phenolphthalein is used as the indicator. (An indicator is a chemical compound that exhibits a change in color as a result of concentration changes occurring near the end point). Since Na_2CO_3 may also react with HCl during the course of the A titration, barium chloride ($BaCl_2$) is added to the liquor prior to titration. $BaCl_2$ reacts with Na_2CO_3 to form $BaCO_3$, a precipitate.

The reactions occurring in Step A are as follows:

$$NaOH + HCl \rightarrow NaCl + H_2O$$

$$Na_2S + H_2O \rightarrow NaSH + NaOH$$

The transfer of Na_2S to NaSH is denoted in our context by (1/2 Na_2S).

In Test B, the active alkali (NaOH + Na_2S) is determined. The main difference between the A and B step is that all of Na_2S is titrated in the B step by the addition of formaldehyde (HCHO) to the liquor prior to B titration and following A titration. Formaldehyde complexes with 1/2 Na_2S or NaSH, releasing the equivalent amount of NaOH so that all of the Na_2S is titrated in the B step.

The reaction between NaSH and formaldehyde is presented as follows (50):

$$HCHO + H_2O \rightarrow HOCH_2OH$$

$$HOCH_2OH + NaSH \rightarrow HOCH_2SH + NaOH$$

The released NaOH is then titrated with HCl using phenolphthalein as the indicator.

In Test C the total alkali is determined: $NaOH + Na_2S + Na_2CO_3$. Following the A and B steps, the indicator (methyl orange) is added to the liquor, and the carbonate (in the form of $BaCO_3$) is determined by titrating the liquor against HCl. The C step was not carried out in this study, since it was not needed for sulfide determination.

The ABC test may either be performed as a continuous procedure or as three separate tests. The procedure described here features the ABC titration as a continuous procedure.

Scope, Apparatus, Reagents, Procedure - ABC Titration

Indicator Method - Manual Technique

Scope

- ABC titration is a colorimetric determination of the amount of sodium hydroxide, sodium sulfide, and sodium carbonate present in kraft white and green liquors.
- Test A is used to determine the amount of effective alkali: $NaOH + 1/2\ Na_2S$.
- Test B is used to determine the amount of active alkali: $NaOH + Na_2S$.
- Test C is used to determine the amount of total alkali: $NaOH + Na_2S + Na_2CO_3$. Test C is omitted if Na_2CO_3 is not a species of interest.
- By mathematical manipulation of the three test results, the amounts of sodium hydroxide, sodium sulfide, and sodium carbonate present in the white or green liquor can be determined.

Reagents/Indicators

- 10% barium chloride
- 0.5N HCl
- 40% formaldehyde

- Phenolphthalein
- Methyl orange

Apparatus

- 50-mL burette and burette stand
- (3) 250-mL Erlenmeyer flasks
- (2) 5-mL, 25-mL pipettes
- 50-mL graduated cylinder

Procedure

- Test A: effective alkali
  - Pipette 5 mL of liquor into a 250-mL Erlenmeyer flask.
  - Add about 50 mL distilled water to the flask.
  - By means of a graduated cylinder, transfer 25 mL 10% barium chloride.
  - Add a few drops of phenolphthalein to the flask.
  - Titrate with standardized 0.5N HCl until the pink color disappears.
  - Record final burette reading as A. Do not refill the burette, since all three titrations are continuous and will not require more than the 50 mL of HCl in the burette.
- Test B: Active alkali
  - Transfer 5 mL 40% formaldehyde into the flask. This causes the pink color to return (pH > 8.3).
  - After waiting for 30 seconds, continue to titrate until the pink color again disappears.
  - Record burette reading as B.
- Test C: Total alkali
  - Add a few drops of methyl orange to the flask.
  - Continue the titration until the first trace of red appears.
  - Record burette reading as C.

Calculations

- Sodium sulfide, as Na_2S

  Na_2S g/L = 2(B-A) x N HCl x 0.031 (eq. wt. Na_2O) x 200 (dil. factor) x 1.258 (conversion Na_2O to Na_2S)

- Sodium hydroxide

  NaOH g/L = (2A-B) x N HCl x 0.031 x 200 x 0.645 (conversion Na_2O to NaOH)

- Sodium carbonate

  $NaCO_3$ g/L = (C-B) x N HCl x 0.031 x 200 x 1.710 (conversion Na_2O to Na_2CO_3)

Modifications

- Sodium sulfide, sodium hydroxide, and sodium carbonate calculations are expressed in the literature as Na_2O. These calculations have been modified by adding a conversion factor. The calculated concentrations can thus be read directly in terms of the species of interest rather than as Na_2O.

pH-Method - Automatic Technique - Mettler DL40 MemoTitrator

Scope

- This procedure describes the ABC sodium sulfide analysis using the Mettler DL40 MemoTitrator.
- The Mettler ABC Titration is an adaptation of the ABC Titration (described on pp. 563-5 of Pulp and Paper Manufacture, Vol. I: The Pulping of Wood), to the Mettler DL40 MemoTitrator.

Apparatus

- Mettler DL40 MemoTitrator
- Mettler GA 40 Printer
- 150-mL beaker, ring stand, and clamp for holding beaker
- (2) 5-mL pipette
- 50-mL graduated cylinder

- Metrohm AGCH 9100, EA 120, or similar glass electrode.
- (2) 50-mL beakers, Celsius thermometer

Chemicals/Reagents

- 0.5N HCl titrant
- 10% barium chloride
- 37% formaldehyde
- pH 7 and pH 10 buffer solutions

Instrument Parameters

- The titration parameters must be entered into the automatic titrator by the operator. The program consists of three parts: Test A; Test B; and Calculation Method.
- Test A
  - Method No.: Arbitrarily selected by operator for instrument storage.
  - Method: End point absolute
  - Reagent No.: Number selected by operator, and reagent characterized and entered according to reagent number, titration factor, reagent concentration, and burette volume.
  - Link to method: Method number selected by operator for Test B.
  - Input code: 100
  - Result unit: -5
  - Constant: 1
  - Max. volume mL: 45
  - Stir time S: 3
  - mV or PX 0/1: 1
  - Trend 1/-1: -1
  - End point absolute: 9.3

- Control band: 2.3
- Delay S: 5

• Test B

- Method No.: Selected by operator
- Method: End point absolute
- Reagent No.: Selected and characterized by operator
- Link to method: Method number selected by operator for the calculation method
- Input code: 1000
- Result unit: -5
- Constant: 1
- Max. volume mL: 10
- Stir time S: 3
- mV or PX 0/1: 1
- Trend 1/-1: -1
- End point absolute: 8.3
- Control band: 2.3
- Delay S: 30

• Calculation method

- Method No.: Selected by operator
- Calculations
- Blank to step: 0
- 1. Result unit -5

  K11 = 1

  K12 = 0

  K13 = 0

- 2. Result unit: -5

  K21 = 0

  K22 = 1

  K23 = 0

- 3. Result unit -9

  K31 = 0

  K32 = 15.6

  K33 = 0

Procedure

- Calibrate the glass electrode using pH buffers 7 and 10 as with Mettler DL40 MemoTitrator instruction manual.
- Set up the burette according to the instruction manual.
- Sample preparation
- Pipette 5 mL of white liquor into a 150-mL beaker.
- Add about 50 mL of distilled water.
- Add 25 mL barium chloride to beaker.
- Mount the sample beaker in the clamp of the ringstand and insert below the stirring mechanism of the instrument.
- Rinse burette tip into waste container according to the instruction manual.
- Mount burette tip in stirring mechanism and into sample beaker.
- Initiate titration for Test A according to the instruction manual, using 0.5N HCl. Titrator automatically carries out Test A to completion.
- Following completion of Test A titration, pipette 5 mL 37% formaldehyde into sample beaker.
- The method for Test B has been recalled automatically following Test A. Initiate Test B titration according to the instruction manual.

Data/Calculation

- Resultant equivalent volumes for Test A and Test B as well as g/L Na_2S are automatically recorded on the GA 40 Printer.

TAPPI STANDARD T 624 os-68

Introduction and Principles

The TAPPI standard is widely used for the determination of sulfide, thiosulfate, and sulfite in white liquor. The procedure is a volumetric analysis based on the use of iodine as a titrant. When iodine is used as a titrant, two methods are distinguished: the iodimetric or direct method and the iodometric or indirect method. The iodimetric method comprises procedures that use a standard solution of iodine to titrate easily oxidized substrates (i.e., substances with lower oxidation potential than the iodine/iodide system). The iodine/iodide system may be presented as follows:

$I_3^- + 2\ e \rightleftarrows 3I^-$

During the iodimetric titration, the above reaction is directed toward the right (i.e., production of iodide). In iodometric methods a substance with higher oxidation potential than the iodine/iodide system oxidizes iodide to iodine (i.e., the reaction shown above is driven to the left). The quantity of iodine formed is then titrated with a standard solution of sodium thiosulfate or arsenic (III) oxide.

The TAPPI procedure is based on the iodimetric or direct method and is divided into three basic steps. The first step comprises the determination of total reducing compounds, "T.R.C." (Na_2S, $Na_2S_2O_3$, Na_2SO_3). The second and third steps consist of the determination of sulfide-free reducing compounds ("S.F.R.C."): $Na_2S_2O_3$, and Na_2SO_3. Steps 2 and 3 are referred to as "S.F.R.C.$_b$" and "S.F.R.C.$_c$,"

respectively. The following section will deal with the chemistry involved in all three steps of the TAPPI Standard Procedure T 624 os-68.

Chemistry of the Tappi Procedure

The determination of the total reducing compounds "T.R.C." involves the addition of a white liquor sample to iodine which has previously been acidified with sulfuric acid. The reactions between iodine and the total reducing compounds, Na_2S, Na_2SO_3, and $Na_2S_2O_3$ in acid media are shown below.

doesn't S go to higher oxidation state?

$$S^{2-} + I_2 \rightleftarrows S + 2I^- \quad (1)$$

$$SO_3^{2-} + I_2 + H_2O \rightleftarrows SO_4^{2-} + 2I^- + 2H^+ \quad (2)$$

$$2S_2O_3^{2-} + I_2 \rightleftarrows S_4O_6^{2-} + 2I^- \quad (3)$$

Following the completion of these reactions, the excess iodine (not used in the oxidation of sulfide, thiosulfate, and sulfite) is then titrated with a standard solution of sodium thiosulfate. The reaction between iodine and sodium thiosulfate is the same as shown above. The course of the titration can be visually followed. The presence of iodine is indicated by a rust brown color. During titration, it is reduced by thiosulfate to form the iodide ions (I^-). Although the iodide species is colorless, the solution assumes a light yellowish color, which becomes lighter to light yellow with further additions of $Na_2S_2O_3$. The end of the titration can be more accurately determined when the indicator, thyodene, is added. Thyodene is a starch indicator used toward the end of the titration to sharpen the end point.

As previously indicated, the second and third steps of the TAPPI procedure involve the determination of $Na_2S_2O_3$ and Na_2SO_3. This is accomplished first by removal of sulfide. Sulfide is removed by adding zinc carbonate ($ZnCO_3$) to the liquor sample. Zinc carbonate is prepared by the addition of zinc sulfate to sodium

carbonate (as described later in the procedure). Zinc carbonate reacts with Na_2S to form ZnS, a precipitate, and Na_2CO_3, as shown by the following equation.

$$ZnCO_3 + Na_2S \longrightarrow ZnS\downarrow \text{ (precipitate)} + Na_2CO_3$$

The precipitated ZnS is then filtered and discarded. The liquor, which is now free from sulfide, is ready for thiosulfate and sulfite determination. The liquor is added to acidified iodine, and the excess iodine is titrated with sodium thiosulfate. The reactions between iodine and sulfite and thiosulfate are the same as shown in Step 1 ("T.R.C." step).

Step 3, which is also performed on sulfide-free liquor, comprises a potentiometric titration with iodine as the titrant. Titration is carried out in alkaline medium. In alkaline medium iodine reacts with water to form hypoiodite (HIO) and iodide as shown.

$$I_2 + H_2O \rightleftarrows HIO + I^- + H^+$$

Hypoiodite then reacts with sodium sulfite and sodium thiosulfate according to the following equations:

$$HIO + Na_2SO_3 \rightleftarrows Na_2SO_4 + H^+ I^-$$

or

$$IO^- + SO_3^{2-} \rightleftarrows SO_4^{2-} + I^-$$

$$4HIO + Na_2S_2O_3 + H_2O \rightleftarrows 2Na_2SO_4 + 4I^- + 6H^+$$

or

$$4IO^- + S_2O_3^{2-} + H_2O \rightleftarrows SO_4^{2-} + 4I^- + H^+$$

From the chemical reactions occurring during "T.R.C.," "S.F.R.C.$_b$," and "S.F.R.C.$_c$" steps, Kesler (51) has explained the calculation of sulfide, sulfite, and thiosulfate concentrations. For convenience we have included the derivation of the calculation in Appendix II.

Scope, Apparatus, Reagents, and Procedures

Scope

- This procedure describes sulfide, thiosulfate, and sulfite analysis of kraft white liquor using TAPPI Standard T 625 os-68 (2).
- Portions of T 624 os-68 have been slightly modified to decrease the time of analysis.

Apparatus

- Büchner funnel and suction flask; each 500 mL
- Wattman No. 40 ashless filter paper
- 50-mL burette and burette stand
- 5, 10, 15, (2) 25-mL pipettes
- 50 and 100 mL graduated cylinders
- (6) 250-mL Erlenmeyer flasks
- 100 and 250-mL volumetric flasks
- Mettler DL40 MemoTitrator
- Mettler GA 40 Printer
- Platinum Electrode
- Saturated Calomel Electrode

Reagents/Indicators

- 0.2N and 0.15N standard iodine solutions
- 0.1N standard $Na_2S_2O_3$
- 20% H_2SO_4
- Thyodene as a starch indicator
- 1M $ZnSO_4$
- 1M Na_2CO_3
- Freshly prepared ammoniacal silver nitrate
- 12M NaOH

Procedure

- Total reducing compounds, "T.R.C." (Na_2S + Na_2SO_3 + $Na_2S_2O_3$)
  - Pipette 25 mL of liquor into a 100-mL volumetric flask. Dilute to mark with distilled water.
  - Pipette 25 mL standardized iodine solution into a 250-mL Erlenmeyer flask.
  - Pipette 5 mL of 20% H_2SO_4 into the flask.
  - Rinse the inside of the flask with about 30 mL distilled water.
  - Pipette 10 mL of the diluted liquor into the flask while vigorously swirling the contents of the flask.
  - Titrate the excess iodine with 0.1N $Na_2S_2O_3$, adding 1 or 2 microspatulas of thyodene when the yellow color has nearly disappeared.
- Sulfide-free reducing compounds, "S.F.R.C." (Na_2SO_3 + $Na_2S_2O_3$)

  Removal of Sulfide
  - Make a preliminary test on an aliquot of the liquor to determine the amount of zinc carbonate required for complete sulfide removal as follows: Pipette 25 mL of liquor into a 250-mL volumetric flask. Add a freshly prepared suspension of $ZnCO_3$ made by mixing 40 mL each of 1M $ZnSO_4$ and 1M Na_2CO_3 to the 250-mL volumetric flask. Mix the contents well by swirling the flask. Dilute to mark with distilled water while gently swirling the contents of the flask. Filter using Büchner funnel, suction flask, and Wattman No. 40 ashless filter paper. Add a drop of freshly prepared ammoniacal silver nitrate to the clear filtrate. If a brown or heavy cloud forms in the filtrate, precipitation is incomplete. Repeat the procedure using ± 5 mL of the original volumes of 1M $ZnSO_4$ and 1M Na_2CO_3 until the amount of $ZnCO_3$ suspension required to completely remove sulfide has been determined.

- Pipette 25 mL of liquor into a 250-mL volumetric flask and add the entire amount of $ZnCO_3$ suspension necessary to completely remove sulfide as found in the preliminary test for complete sulfide removal. Dilute to mark with distilled water while gently swirling the contents of the flask.
- Filter using Büchner funnel, suction flask, and Wattman No. 40 ashless filter paper.

• Oxidation with Iodine ("S.F.R.C.$_b$")

- Pipette 15 mL of standardized 0.2N iodine solution into a 250-mL Erlenmeyer flask.
- Pipette 5 mL of 20% H_2SO_4 into the flask.
- Pipette 25 mL of the clear filtrate into the acidified iodine while vigorously swirling the contents of the flask.
- Titrate the excess iodine with 0.1N $Na_2S_2O_3$, adding 1 or 2 microspatulas of thyodene near endpoint (faint yellow color).

• Oxidation with Hypoiodite ("S.F.R.C.$_c$")

• Instrument parameters using Mettler DL40 MemoTitrator

- Method No: Selected by operator
- Method: End point absolute
- Reagent No.: Selected by operator (0.15N iodine)
- Link to method: 0 (link to calculation method optional)
- Input code: 1000
- Result unit: -5
- Constant: 1
- Max. volume mL: 10
- Stir time S: 30
- mV or PX 0/1: 0
- Trend 1/-1: 1

- End point absolute: 0
- Control band: 30
- Delay S: 45

• Set up burette with 0.15N iodine according to Mettler DL40 instruction manual.

• Add 50 mL 12M NaOH to sample cup.

• Pipette 25 mL of clear filtrate into sample cup.

• Rinse burette tip into waste beaker using "Rinse Tip" function of the instrument. Mount burette tip into sample medium.

• Initiate titration according to the instruction manual using 0.15N iodine solution and platinum and saturated calomel electrodes.

• Titration is automatically run to completion (end point 0 mV) and the resultant eq. volume of 0.15N iodine used is automatically recorded on the GA 40 Printer. (Note: This titration may also be performed manually using the millivolt function of a pH meter and with magnetic stirring as called for in TAPPI T 624 os-68.)

Data/Calculations

• Record all data as needed.

• Calculations.

• Total reducing compounds, "T.R.C."

$$\text{"T.R.C." eq/liter} = \frac{(\text{mL } I_2 \times N I_2) - (\text{mL } Na_2S_2O_3 \times \text{N } Na_2S_2O_3)}{2.5}$$

• Sulfide-free reducing compounds, "S.F.R.C."

$$\text{"S.F.R.C.}_b\text{" eq/liter} = \frac{(\text{mL } I_2 \times N I_2) - (\text{mL } Na_2S_2O_3 \times \text{N } Na_2S_2O_3)}{2.5}$$

$$\text{"S.F.R.C.}_c\text{" eq/liter} = \frac{\text{mL } I_2 \times N I_2}{2.5}$$

- Sodium Sulfide

$$Na2S\ g/L = \frac{("T.R.C." - "S.F.R.C.b") \times 78.1}{2}$$

- Sodium thiosulfate

$$Na2S2O3\ g/L = \frac{("S.F.R.C.c" - "S.F.R.C.b") \times 158.1}{7}$$

- Sodium sulfite

$$Na_2SO_3\ g/L = \frac{"S.F.R.C._c" - \left(\frac{Na_2S_2O_3 \times 8}{158.1}\right) \times 126.1}{2}$$

Modifications of T 624 os-68

- The volume of liquor used in determining sulfide-free reducing compounds was changed from 50 mL to 25 mL.
- As a result of the modification in sample dilution, the denominator in the determination of both "S.F.R.C.b" and "S.F.R.C.c" was changed from 5 to 2.5.
- The starting volumes of 1M $ZnSO_4$ and 1M Na_2CO_3 were changed from 15 mL to 40 mL.
- In the preliminary test for complete removal of sulfide, the filtration step was added to decrease the time needed to make the determination.

APPENDIX V

POTENTIOMETRIC TITRATION

Scope, Apparatus, Reagents, and Procedures

Automatic Technique - Metrohm E636 Titroprocessor

Titrant - Silver Nitrate ($AgNO_3$)

Scope

- This procedure describes a method of sodium sulfide analysis of kraft weak black liquor using the Metrohm E636 Titroprocessor equipped with a Dosimat E635 titrating stand and an E649 magnetic stirrer.
- The method is an adaptation of TAPPI T 625 ts-64 sulfide analysis to the E636 Titroprocessor.
- The E636 Titroprocessor automatically performs and plots a potentiometric sulfide analysis using 0.1000M $AgNO_3$ as titrant.

Apparatus

- Metrohm E636 Titroprocessor
- Metrohm Dosimat E635 titrating stand
- Metrohm E649 magnetic stirrer
- Orion 94-16A sulfide-ion selective and 90-02 double junction reference electrodes
- 250-mL beaker
- 25-mL graduated cylinder
- 5-mL and 10-mL pipettes
- EA 1122/1 control card
- EA 1122/2 control card (calculation card optional)

Reagents

- 20% NaOH
- 1:99 ammonia
- 0.1000M $AgNO_3$

Instrument Parameters

- The instrument parameters are set by blackening the appropriate boxes on the EA 1122/1 control card.
- Control card markings
- Operation mode: Boxes 2 & 3
- Temp./°C: Darken applicable boxes for rows 1,2, & 3
- Kinetics: Box 0 (controlled drift of 0.469 mV/min)
- Meas. pt. dens.: Box 3
- Start V/mL: Row 1: Leave blank (may be modified for second run of a duplicate determination).
  Row 2: Leave blank.
- Stop or EP, U/mV, pH: Row 1: Box 0
  Row 2: Box 4
  Row 3: Box 0
  Row 4: Box 0
- Stop V/mL: Row 1: Box 9
  Row 2: Box 9
- Stop EP No.: Leave all boxes blank.
- Scale U/mV, pH BEG: Row 1: Box 0
  Row 2: Box 9
- Scale U/mV, pH END: Row 1: Box 0
  Row 2: Box 4

Procedure

- Add 25 mL of 20% NaOH to a 250-mL beaker
- Pipette 10 mL of 1:99 ammonia into the beaker
- Dilute to 125 mL with distilled water
- Place the beaker on the E649 magnetic stirrer and adjust the rate of stirring so that there is just the beginning of a vortex.
- Lower the electrodes into the solution to a depth of about one inch.
- Pipette 5 mL of weak black liquor into the sample medium.
- Rinse the burette tip with distilled water over a waste beaker, then mount the burette tip into the sample medium.
- Initiate titration
- Feed the Ea 1122/1 control card into the instrument. If a calculation method is to be programmed in conjunction with the titration, feed the 1122/2 card into the instrument also.
- A titration curve is plotted during the sample run, and the end point location is identified. The equivalent volume of titrant at end point is listed. If an E 1122/2 calculation card is used, the resulting concentration and calculation constant are listed also.

Data/Calculations

- Data
  - A complete list of the summative increment volumes and their corresponding potentials may be obtained by using the "Measuring Point List" function of the instrument.
  - By using the "Report" key of the instrument, a report of parameter values set on and the titration conditions is listed.

- Calculation

$$Na_2S\ g/L = \frac{\frac{0.1000\underline{M}\ AgNO_3}{1000\ mL} \times 2 \times mL\ HgCl_2 \times 39.025}{0.005\ liter\ sample}$$

- Automatic calculation of the above equation may be obtained by utilization of the EA 1122/2 control card.

Modifications

- The following modifications of the TAPPI T 625 ts-64 sulfide analysis have been made:
- The beaker size was changed from 800 mL to 250 mL.
- The volume of 20% NaOH was changed from 100 mL to 25 mL.
- The volume of 1:99 ammonia was changed from 35 mL to 10 mL.
- The sample medium was changed from 500 mL to 125 mL.
- An Orion 90-02 double junction reference electrode was used instead of a "high" pH glass electrode.

Titrant - Mercuric chloride (HgCl2)

Scope

- This procedure describes a method of sodium sulfide analysis of kraft weak black liquor using the Metrohm E636 Titroprocessor equipped with a Dosimat E635 titrating stand and an E649 magnetic stirrer.
- The E636 Titroprocessor automatically performs and plots a potentiometric sulfide analysis using 0.1000M HgCl2 titrant.

Apparatus

- Metrohm E636 titroprocessor
- Metrohm Dosimat E635 titrating stand
- Metrohm E649 magnetic stirrer
- Orion 94-16A sulfide-ion selective and 90-02 double junction reference electrodes

- 250-mL beaker
- 50-mL graduated cylinder
- 5-mL transfer pipette
- EA 1122/1 control card
- EA 1122/2 control card (calculation card optional)

Reagents

- 4M NaOH
- Na_2SO_3 crystals
- 0.1000M $HgCl_2$

Instrument Parameters

- The instrument parameters are set by blackening the appropriate boxes on the EA 1122/1 control card.
- Control card markings
- Operation mode: Boxes 0, 1, 2, 3
- Temp./°C: Darken applicable boxes for rows 1, 2, and 3
- Kinetics: Box 0 (controlled drift of 0.469 mV/min)
- Meas. Pt. Dens.: Box 0 (0.1-mL increments with 20-mL burette)
- Start V/mL: Row 1: Leave blank (may be modified for second run of a duplicate determination).
  Row 2: Leave blank.
- Stop or EP, U/mV, pH: Row 1: Box 0
  Row 2: Box 3
  Row 3: Box 0
  Row 4: Box 0
- Stop V/mL: Row 1: Box 9
  Row 2: Box 9
- Stop EP No.: Leave all boxes blank.

- Scale U/mV, pH BEG: Row 1: Box 0
  Row 2: Box 9
- Scale U/mV, pH END: Row 1: Box 0
  Row 2: Box 3

Procedure

- Add 40 mL of 4M NaOH to a 250-mL beaker
- Add 5 g Na_2SO_3 crystals and a Teflon-covered magnetic stirring bar to the beaker.
- Dilute to mark with distilled water. Place the beaker on the magnetic stirrer and dissolve the crystals. After the Na_2SO_3 crystals have dissolved, adjust the stirring rate just short of creating a vortex in the solution.
- Pipette 5 mL of black liquor into the beaker.
- Rinse the burette tip with distilled water over a waste beaker, then mount the burette tip into the sample medium.
- Feed the EA 1122/1 control card into the instrument. If a calculation method is to be programmed in conjunction with the titration, feed the 1122/2 card into the instrument also.
- Initiate the titration according to the instruction manual.
- A titration curve is plotted during the sample run, but the end point location is not identified on the curve. The equivalent volume of the end point is listed. If an E 1122/2 calculation card is used, the resulting concentration and calculation constant are listed also.

Data/Calculations

- Data
  - A complete list of summative increment volumes, their corresponding potentials, and the potential change per increment addition may be

obtained by using the "Measuring Point List" function of the instrument.

- By using the "Report" key of the instrument, a report of parameter values set on and the titration conditions is listed.

• Calculation

$$Na_2S\ g/L = \frac{\frac{0.1000M\ HgCl_2}{1000\ mL} \times mL\ HgCl_2 \times 78.04\ g\ Na_2S/Mole}{\text{Volume (in liters) of sample}}$$

• Automatic calculation of the above equation may be obtained by utilization of the EA 1122/2 control card.

ABC TITRATION

Scope, Apparatus, Reagents, and Procedures

pH-Method - Metrohm E636 Titroprocessor

Scope

• This procedure describes sulfide analysis of kraft weak black liquor using the Metrohm E636 Titroprocessor equipped with a Dosimat E635 titrating stand and an E649 magnetic stirrer.

• The manual ABC titration is automated by setting pH end point titration parameters on the 1122/1 control card.

Apparatus

• Metrohm E636 Titroprocessor

• Metrohm Dosimat E635 titrating stand

• Metrohm E649 magnetic stirrer

• Metrohm EA 120 glass electrode, or equivalent

• 25-mL graduated cylinder

• 150-mL beaker

- Transfer pipettes of various volumes
- EA 1122/1 control card
- EA 1122/2 control card (calculation card optional)

Reagents/Buffers

- 10% barium chloride
- 37% formaldehyde
- 0.5N HCl (standardized)
- pH 7 and pH 10 buffer solutions

Instrument Parameters

- The instrument parameters are set by blackening the appropriate boxes on the EA 1122/1 control card
- Control card markings
  - 1122/1 Card 1 (pH calibration)
  - Temp/°C: Darken applicable boxes for rows 1, 2, & 3
  - Kinetics: Box 2
  - No other boxes (modifications) are marked. The calibration function is controlled by the standard "card code" located at the bottom of the EA 1122/1 control card.
  - 1122/2 Card 2 (titration parameters)
  - Operation mode: Boxes 1, 2, 3, 8, & 9 (EP-TITR: MPD var, NORM, with pH calibration; kinetics D)
  - Temp./°C: Darken applicable boxes for rows 1, 2, & 3
  - Kinetics: Box 2 [1.875: drift/(mV/min)]
  - Meas. Pt. Dens.: Box 0
  - Start V/mL: Row 1: Box 0
    Row 2: Box 0

- Stop or EP, U/mV, pH: Row 1: Leave blank
  Row 2: Box 9
  Row 3: Box 3
  Row 4: Leave blank
  } Test A

  Row 1: Leave blank
  Row 2: Box 8
  Row 3: Box 3
  Row 4: Leave blank
  } Test B

- Stop V/mL: Row 1: Box 9
  Row 2: Box 0
- Stop EP No.: Leave blank

• Scale U/mV, pH BEG: Row 1: Box 1
  Row 2: Box 3

• Scale U/mV, pH END: Row 1: Leave blank
  Row 2: Box 7

Procedure

• Calibrate the pH electrode with pH 7 and pH 10 buffers using the EA 1122/1 Card 1 control card according to the instruction manual.

• Preparation of sample

  - Add 50 mL distilled water and a Teflon-covered stirring bar to a 150-mL beaker. Set the beakers on the E649 magnetic stirrer. Activate the stirrer and adjust the stirring speed so as not to create a vortex in the liquid.

  - Pipette a volume of weak black liquor (10-50 mL) into the beaker. Add 25 mL of 10% barium chloride to the beaker, and, if necessary, readjust the stirring speed.

- Rinse the burette tip with distilled water over a waste beaker, then mount the burette tip into the sample medium.

• Initiate Titration (Test A)

- Feed the EA 1122/1 card (titration parameters) into the instrument.
- Initiate the titration according to the instruction manual. The sample is automatically titrated to a pH end point of 9.3. A titration curve is plotted during the sample run, with a listing of the end point equivalent volume for Test A.
- Pipette 5 mL of 37% formaldehyde into the sample beaker and wait 30 sec.

• Initiate Titration (Test B)

- Feed an EA 1121 control card identical to the card for Test A, with the exception of a modification of the pH end point into the instrument. (The pH end point is modified from 9.3 to 8.3.)
- Initiate the titration according to the instruction manual. The sample is automatically titrated for a second time to a pH end point of 8.3. A titration curve is plotted during the sample run, with a listing of the end point equivalent volume for Test B.

Data/Calculations

• Data

- By using the "Report" key of the instrument, a report of parameter values set on and the titration conditions is listed. These may be supplemented with handwritten notes.
- A complete list of all summative increment volumes and their corresponding pH values can be obtained by using the "Measuring Point List" function of the instrument.

• Calculations

$$Na_2S\ g/L = \frac{\frac{0.5N\ HCl}{1000\ mL} \times 2\ (Vol.\ Test\ B) \times 39.02\ g\ Na_2S}{Volume\ (liters)\ sample}$$

TAPPI STANDARD 625 ts-64

Introduction and Principles

The TAPPI method is comprised of manual potentiometric titration for the determination of Na_2S, $Na_2S_2O_3$, and Na_2SO_3.

The procedure consists of three steps. In Step I, sodium sulfide is determined by the use of $AgNO_3$ as the titrant. The reaction between Na_2S and $AgNO_3$ may be presented as follows: $Na_2S + AgNO_3 \rightarrow Ag_2S + NaNO_3$.

In Step II, sulfide is removed by reacting it with zinc carbonate as previously described in TAPPI 624 os-68. Following filtration of ZnS, the filtrate is used for the determination of sodium sulfite and sodium thiosulfate. This is accomplished by potentiometric titration using the HgCl2 as the titrant. The reactions between HgCl2 and Na2SO3 and Na2S2O3 may be presented as follows:

$$2\ SO_3^{2-} + Hg^{2+} \rightarrow [Hg\ (SO_3^{2-})_2]^{-2}$$

$$2\ S_2O_3^{2-} + Hg^{2+} \rightarrow [Hg\ (S_2O_3^{-2})]^{-2}$$

Step III comprises the determination of only sodium thiosulfate. This is done by removal of sulfite from the sulfide-free filtrate by the addition of formaldehyde. Formaldehyde complexes with sulfite to form the hydroxy sulfonate CH_2OHSO_3Na. The formation of the sulfonate ties down the sulfite so that only thiosulfate can be determined by manual potentiometric titration with HgCl2 as the titrant.

Scope, Apparatus, Reagents, and Procedures

Scope

- This procedure describes sodium sulfide, thiosulfate, and sulfite analysis of kraft weak black liquor using TAPPI Standard T 625 ts-64.
- Portions of T 625 ts-64 have been slightly modified.

Apparatus

- 250-mL, 600-mL, and 800-mL beakers
- pH meter, with a milliwatt scale
- 10-mL burette and burette stand
- Büchner funnel and suction flask, each 500 mL
- Orion 94-16A sulfide-ion selective and Orion 90-02 double junction reference electrodes
- Corning No. 476060 Platinum and Corning No. 476002 Saturated Calomel Electrodes or equivalent
- Wattman No. 40 ashless filter paper
- 50-mL and 100-mL graduated cylinders
- (2) 5-mL and (2) 100-mL transfer pipettes, disposable pipette
- 100-mL volumetric flask
- Glass (pH) electrodes

Reagents

- 20% NaOH
- 1:99 ammonia
- 0.1000M $AgNO_3$
- 0.05M $HgCl_2$
- Glycerin
- 1M $ZnSO_4$
- 1M Na_2CO_3

- Mercury, c.p.
- 2:5 acetic acid
- 37% formaldehyde
- Freshly prepared ammoniacal silver nitrate

Procedure

- Sodium Sulfide
- Add 100 mL of 20% NaOH and 35 mL of 1:99 ammonia to an 800-mL beaker. Dilute to 500 mL with distilled water. Place the beaker on a magnetic stirrer and adjust the rate of stirring to create just the beginning of a vortex.
- Place the sulfide-ion selective and double junction reference electrodes about 1 inch deep into the solution.
- Pipette 5 mL of weak black liquor into the solution.
- Titrate the sample potentiometrically with 0.1000M $AgNO_3$.
- Add the titrant in fixed increments of volume.
- Record the summative volume increments and their corresponding steady millivolt readings. The millivolt reading is considered stable if there is no millivolt change within 30 seconds, as monitored by a stop watch.
- At end point, there will be a slow but comparatively large change in the millivolt reading, in the magnitude of 100 millivolts or more.
- Sodium Sulfite and Sodium Thiosulfate
- Precipitation of sulfide
  - Add 50 mL of glycerin to a nitrogen-filled 1000-mL volumetric flask.
  - Pipette 100 mL of weak black liquor into the flask.
  - Add 400 mL of freshly prepared $ZnCO_3$ suspension made by mixing 200 mL each of 1M $ZnSO_4$ and 1M Na_2CO_3 in a 600-mL beaker. Mix the contents by swirling the flask, dilute to mark with O_2-free distilled water, and mix again.

- Allow the mixture to settle until the bulk of the solids is in the bottom of the flask.
- Withdraw the cloudy supernatant liquid with a 100-mL pipette until it is completely withdrawn. Filter by means of a Büchner funnel, suction flask, and Wattman No. 40 ashless filter paper. Discard the first 100 mL of filtrate.
- Pour a small portion of the filtrate into a small test tube and check for complete sulfide removal with a drop or two of freshly prepared ammoniacal silver nitrate. If a heavy cloud develops, incomplete sulfide removal is indicated, and the sulfide removal procedure must be repeated using larger amounts of zinc sulfate and sodium carbonate.

• Sulfite plus Thiosulfate

- Place mercury to a depth of about 1/4-inch in a 250-mL beaker.
- Pipette 100 mL of clear filtrate into the beaker and place on a magnetic stirrer.
- Using a glass pH electrode, adjust the pH to between 7.0 and 7.5 by adding 2:5 acetic acid with a disposable pipette.
- Place the platinum and saturated calomel electrodes into the solution. The calomel electrode must not touch the mercury pool; the platinum electrode must be submerged in the mercury. Adjust the rate of stirring so that a vortex is not created. Record the initial millivolt reading.
- Titrate the sample with 0.0500M $HgCl_2$, using fixed volume increments. Record the summative volume increments and their corresponding millivolt readings. A large millivolt change should occur at end point.
- Plot the data on linear coordinates with volume $HgCl_2$ as the abscissa and emf. as the ordinate. Determine the exact amount of $HgCl_2$ used at the

end point by projecting the inflection point in the titration curve to intersect the abscissa. Record this volume of $HgCl_2$ as volume A.

- Thiosulfate
  - Proceed with this determination exactly as for determination of the sulfite and thiosulfate above with the following exception: immediately after adjusting the pH, add 5 mL of 37% formaldehyde, stir, and wait 5 minutes before proceeding with the titration.
  - Record the volume of $HgCl_2$ used as volume B. (Note: The mercury pool need not be renewed for each titration. Decant the liquid and wash several times with distilled water. Remove any remaining liquid with a disposable pipette.)

Data/Calculation

- Record all data as indicated in the procedure.
- Calculations
  - Sodium Sulfide

$$Na_2S\ g/L = \frac{\frac{0.1000\ AgNO_3}{1000\ mL} \times mL\ AgNO_3 \times 39.025}{0.005\ liter\ sample}$$

  - Sodium Sulfite

$$Na_2SO_3\ g/L = \frac{2\left[\left(\frac{50\ mM}{1000\ mL} \times A\ mL\ HgCl_2\right) - \left(\frac{50\ mM}{1000\ mL} \times B\ mL\ HgCl_2\right)\right] \times 126\ g\ Na_2SO_3/mol \times 10\ (dil.\ factor)}{100\ mL\ sample}$$

$$= \left[\left(\frac{50\ mM}{1000\ mL} \times A\ mL\ HgCl\ \right) - \left(\frac{50\ mM}{1000\ mL} \times B\ mL\ HgCl\ \right)\right] \times 25.2$$

- Sodium thiosulfate

$Na_2S_2O_3$ g/L =

$$\frac{2 \times \frac{50 \text{ mM}}{1000 \text{ mL}} \times B \text{ mL } HgCl_2 \times 158 \text{ g } Na_2S_2O_3/\text{mol} \times 10 \text{ (dil. factor)}}{100 \text{ mL sample}}$$

$$= \text{"B" mL } HgCl_2 \times 1.58$$

Modifications

- For sulfide determinations, the Orion 90-02 electrode is used instead of a "high" pH glass electrode.
- For sulfite and thiosulfate determinations, magnetic stirring is used instead of electric stirring, although electric stirring should perform at least equally as well.
- 400 mL of ZnC03 was used for precipitation of sulfide instead of the 300 mL as called for in TAPPI T 625 ts-64.

APPENDIX VI

UV SPECTROPHOTOMETRIC METHOD

INTRODUCTION AND PRINCIPLES

Spectrophotometric methods are based on absorption of light energy by a substance to be identified or analyzed. The absorption measurement involves determination of the decrease in the intensity or power of electromagnetic radiation as it passes through an absorbing medium of known dimensions. During absorption, the absorbing substance (in the form of ion, atom, or molecule) is being raised to a higher energy level. The state of the substance at the high-energy level is called the excited state. The substance remains at the excited state for a brief period (10^{-8} to 10^{-9} seconds) and then returns to its former state. The energy released as a result of the return of the substance is called the excitation energy. This energy is lost ordinarily as heat. Since the amount of heat released is so small as to be undetectable, minimal disturbance is created in the system. This is considered an advantage of the absorption methods.

According to the type of electromagnetic radiation absorbed, absorption methods are characterized or named. The types of electromagnetic radiation include x-ray, ultraviolet, visible, infrared, microwave, and radio frequency. In this report we will only be concerned with ultraviolet radiation.

UV Region and Beer's Law

The ultraviolet region of electromagnetic radiation "light energy" ranges between 200 and 400 nm. In our study a wavelength of 280 nm was chosen. The choice was based on absorbancy experiments of polysulfide by Teder (53), who investigated the wavelength range of 210 to 500 nm (in the UV and visible region) and found that the influence of hydroxyl ion concentration is negligible at 280 nm wavelength. The choice of a particular wavelength has two advantages (54): 1) the measurements are

less sensitive to uncertainties resulting from inability to reproduce precisely the wavelength setting of the instrument; 2) good adherence to Beer's law can be expected.

Beer's law is expressed as follows:

$$\log \frac{P_o}{P} = \varepsilon\, bc = A$$

where

P_o = light entering the solution

P = light leaving the solution

c = concentration of the absorbing species

b = length of light path

ε = a constant determined by the nature of the absorbing substance and the wavelength of light

A = absorbance

Concentration Determination

To determine precisely the concentration of an unknown sample, Beer's law (the direct proportionality between concentration and absorbance) is to be obeyed. This can be investigated by plotting the concentration of known standards vs. their absorbance measurements. If a straight line is obtained, adherence to Beer's law is indicated. Figure 8 shows a plot of known polysulfide sulfur concentration vs. absorbance. From this plot, the unknown concentrations of polysulfide in liquor samples may be determined. Since, at a specified wavelength the individual property of the substance is constant (i.e., ε is constant), and since the light path length b (cuvette or solution container) is fixed, the relationship between absorbance A and the concentration c may be expressed as:

$$A = Kc$$

where $K = \varepsilon b$

Change bottom legand from Polysulfide sulfur concentration (g/l)
to Polysulfide sulfur concentration (g/L)

Figure 8. A plot of polysulfide sulfur concentration vs. absorbance.

60 g/mol NaOH
31.2 g/mol Na2S

7.8
4 | 31.2
28
32

1 g
0.5 g

500 mL
250 mL 160 g/mol NaOH + 31.2 g/mol Na2S
= 40 g NaOH and 7.8 g Na2S
+ .5 g

This relationship means that the extent to which light is absorbed depends only on the concentration of absorbing molecules.

Scope, Apparatus, Reagents, and Procedures

Scope

- This procedure describes a method of polysulfide sulfur analysis of kraft white liquor using a Perkin-Elmer Model 576 ST spectrophotometer.
- The absorbancy unit reading of a sample is compared with a standard "Absorbancy/Concentration" calibration chart to determine the concentration of polysulfide sulfur present.

Apparatus

- Perkin-Elmer Model ST spectrophotometer
- (2) cuvettes, 10-mm light path
- 100-mL and 250-mL volumetric flasks
- Transfer pipettes, various volumes as required

Solutions

- 3M NaCl in 10^{-2}M NaOH, oxygen-free

Preparation of Calibration Chart

- A standard calibration chart is prepared only once. All future polysulfide sulfur determinations are made by comparing the sample absorbancy readings with the original calibration chart.
- Preparation of NaOH/Na_2S Stock Solution
  - Add approximately 300 mL of oxygen-free distilled water to a 500-mL volumetric flask.
  - Add 80 g NaOH and dissolve using magnetic stirring. Purge with O_2-free nitrogen while dissolving the NaOH pellets. Allow the solution to cool to room temperature while continuing the nitrogen purge.

- Add 48.0 g $Na_2S \cdot 9H_2O$ crystals that have been thoroughly rinsed with distilled water and blotted dry before weighing. Dissolve using magnetic stirring and purging with O_2-free nitrogen.
- Dilute to mark using O_2-free distilled water. Mix well. The solution yields approximately 160 g/L NaOH and 31.2 g/L Na_2S.

• Preparation of Polysulfide Stock Solution

- Transfer 250 mL of oxygen-free stock NaOH/Na_2S to a second 500-mL volumetric flask. Stopper tightly.
- Add 0.500 g elemental sulfur. Dissolve using magnetic stirring at 50-70°C while continuing to purge with O_2-free nitrogen.
- Cool to room temperature while purging with O_2-free nitrogen.
- Dilute to mark with O_2-free distilled water. Mix well. Place a layer of heavy mineral oil on the top of the solution. The solution yields 1.000 g/L polysulfide sulfur and approximately 80 g/L NaOH and 15.6 g/L Na_2S.

• Preparation of Polysulfide Standards

- To each of the flasks used for dilution, add O_2-free 3M NaCl in 10^{-2}M NaOH to about 50% of the flask volume.
- Pipette the following amounts of polysulfide stock solution into each of the volumetric flasks:

Flask No	1	2	3	4	5	6	7	8	9
Vol. Flask	100	250	250	100	250	100	250	100	250
mL Stock S°	10	20	15	5	10	3	5	1	2
g/L S°	0.100	0.080	0.060	0.050	0.040	0.030	0.020	0.010	0.008

- Dilute to mark with O_2-free 3M NaCl in 10^{-2}M NaOH. Mix well, then add a thin layer of heavy mineral oil.

- Preparation of Reference Solution
  - To the first 500-mL volumetric flask containing 250 mL of 160 g/L NaOH and 31.2 g/L Na_2S, add O_2-free 3M NaCl in 10^{-2} NaOH until diluted to mark. Mix and add a thin layer of heavy mineral oil to the surface of the solution.
  - Obtain absorbancy readings for all polysulfide standards.
  - Zero the instrument.
  - Place the reference solution into both the sample and reference cuvettes.
  - Adjust the absorbancy reading to $\pm$ 0.000 by the OA/100% adjustment knob.
  - Pipette 3 mL of polysulfide standard from Flask No. 1 into a clean sample cuvette and obtain an absorbancy reading. Record the absorbancy. Repeat for the remaining standards.
  - Prepare a calibration chart with absorbancy units located on the ordinate and g/L 5° concentration on the abscissa. Determine the concentration linearity range by drawing a straight line through the data points. The lower and higher concentrations may be nonlinear with respect to the absorbancy units obtained.

Procedure

- Preparation of sample
  - Sample dilutions must be made so that the diluted concentrations fall within the linearity range of the calibration chart. If the relative polysulfide concentration of the sample is unknown, more than one diluted sample may be necessary.
  - To each volumetric flask, add O_2-free 3M NaCl in 10^{-2} NaOH to 50% of flask volume.
  - Pipette an amount of liquor into the flask.
  - Dilute to mark with O_2-free 3M NaCl in 10^{-2} NaOH. Stopper and mix well.

- Place a thin layer of heavy mineral oil on top of the liquid con nt of the flask.

• Obtain absorbancy readings

- Turn on the power switch of the spectrophotometer.
- Turn on the UV lamp.
- Allow 15 minutes for the instrument to warm up.
- Calibrate the instrument.
- Close the sample shutter (front lever forward).
- Set the "Source" knob to UV.
- Set the wave length to 285 nm with the slew buttons.
- Flip the calibrate switch to the "On" position.
- Turn the calibrate knob until the digital reading is $\pm$ 0.00, with flickering of the $\pm$ signs.
- Flip the calibrate switch back to the "Off" position.
- Open the sample shutter with the sample shutter lever.

• Zero the instrument.

- Place reference solution(3M NaCl in 10^{-2} NaOH) in both cuvettes.
- Place the cuvettes in the sample and reference compartments, with the frosted glass oriented toward the operator.
- Close the sample/reference compartment door.
- Set the "OA" switch to manual.
- Push the "ABS" (absorbancy) button "In."
- Turn the "OA/100%" adjustment knob until the display reading is 0.000.
- Depress "%T" button slightly to disengage "ABS" button.

• Obtain sample absorbancy reading.

- Remove the sample cuvette containing reference solution from the sample compartment and empty the cuvette.

- Rinse the cuvette three times with distilled water, then once with either acetone or ethyl alcohol. Allow to dry. If desired, drying may be hastened with an electric blow dryer.
- Pipette 3 mL of sample into the sample cuvette and place the cuvette into the sample compartment with the frosted glass oriented toward the operator. Close the compartment door.
- Press the "ABS" button to the "In" position and record the absorbancy reading.
- Depress "%T" button slightly to disengage "ABS" button.
- Repeat previous steps of "obtain sample absorbancy reading" for all samples to be analyzed.

• Instrument shutdown

- Turn the UV lamp to the "Off" position and wait until the "Low Energy" light comes on.
- Set the main "Power" switch to the "Off" position.

Data/Calculation

• Record the sample dilution factors and the absorbancy readings obtained for each sample.

• Locate the absorbancy reading of the sample on the ordinate of the calibration chart. Locate the corresponding chart concentration on the abscissa.

• g/L polysulfide sulfur, as sulfur = chart concentration x dilution factor

$$\text{Example: } 0.030 \times \frac{100 \text{ (volume flask)}}{5 \text{ (vol. conc. liquor)}} = 0.6 \text{ g/L } 5°$$

Modifications

• If colored substances in the sample other than polysulfide are present, a reference solution may be prepared by treating the same volume of sample (as in the sample) with sulfite crystals at 50°C. After cooling, the

treated sample is diluted with O_2-free 3M NaCl in 10^{-2}M NaOH in the same proportion as the sample and then used as the reference.

DIFFERENTIAL PULSE POLAROGRAPHIC METHOD

Scope, Apparatus, Reagents, DPP Parameters, and Procedures

Scope

- This procedure describes a method of polysulfide analysis of kraft white liquor using differential pulse polarography (DPP).
- Two thiosulfate analyses are performed. The first is a thiosulfate analysis of the white liquor. The second consists of a thiosulfate analysis following the reduction of polysulfide with sodium sulfite.
- The thiosulfate concentrations of the untreated sample and the sample treated with sulfite are used to calculate the concentration of polysulfide sulfur present in the liquor.

Apparatus

- PAR Model 384 Polarographic Analyzer.
- PAR Model 303 Static Mercury Drop Electrode
- (2) Pyrex gas scrubbing towers. Tower I is filled with vanadous chloride solution containing zinc amalgam at the bottom of the tower. Tower II is filled with 0.5M acetate buffer solution, identical to the polarographic medium. Tower I is located between a tank of O_2-free nitrogen and tower II. Tower II is located between Tower I and the Model 303 SMDE.
- Gilson PIPETMAN adjustable digital microliter pipette, or equivalent.
- Houston Hi-Plot Digital Plotter, or equivalent digital plotter.
- (2) 100-mL volumetric flasks
- 10-mL and (2) 25-mL tranfer pipettes.
- 150-mL beaker
- Magnetic stirrer with hot plate, Celsius thermometer.

Reagents

- 0.5M acetate buffer
- Standardized 0.1N $Na_2S_2O_3$
- Na_2SO_3 crystals

Preparation of $Na_2S_2O_3$ Polarographic Standard

- Pipette 25 mL of 0.1N $Na_2S_2O_3$ into a 100-mL volumetric flask.
- Dilute to mark with distilled water and mix well.
- $Na_2S_2O_3$ g/L = Normality $Na_2S_2O_3$ (0.1N) x 158.1

  (The dilution factor does not need to be accounted for, since the sample dilution is the same as the standard.)

Preparation of Sample

- Pipette 25 mL of liquor into a 100-mL volumetric flask.
- Dilute to mark with distilled water and mix well.

Preparation of Treated Sample

- Pipette 25 mL of white liquor into a 150-mL beaker.
- Add 0.5 g Na_2SO_3 crystals.
- Stir using magnetic stirrer and hot plate at 50°C until color becomes clear. Allow to cool.
- Quantitatively transfer the treated sample to a 100-mL volumetric flask and dilute to mark with distilled water.

DPP Parameters

- Technique selection: Differential pulse polarography
- Run parameter keys

  Initial potential: -400 millivolts

  Final potential: zero millivolt

  Pulse height: 0.025 V

  Sample number: Entered for each sample run

- Purge time: Blank: 240 sec

  Sample: 420 sec

  Standard: 180 sec

- Date: Day, month, and year sample is analyzed.
- Scan rate: 4 mV/sec (set by "DROP TIME" and "SCAN INCREMENT" keys)
- Drop time: 1.0 sec
- Scan increment: 4 mV
- Other keys: Do not apply for DPP
- Playback and Calculation Parameter Keys
  - Calculation method: Standard addition
  - Peak potential: Value entered after initial playback of standard
  - Peak concentration: Value entered after initial playback of standard
  - Clear standard data: Key pressed prior to next sample analysis followed by pressing the "Yes" key
  - Override: 10 Autoplayback: Yes

    11 Plot run data: No

    12 Plot playback data: Yes

    13 Plot results: Yes

    14 RS 232 playback data: No

    15 RS 232 results: No

    16 Real time data smoothly: Yes

    17 Invest playback data: No
  - Tangent fit: Yes
  - Blank subtract: Yes
  - Other keys: Not used

Procedure

- Set all DPP parameters according to Section 7. ?????????
- Sample Analysis (untreated)
  - Pipette 10 mL of 0.5M acetate buffer into the sample cup and mount it onto the Model 303 SMDE.
  - Run a "Blank" on the 0.5M acetate buffer polarographic medium.
  - Press the "Blank" key.
  - Press the "Run" key.
  - The polarographic medium is automatically purged with oxygen-free nitrogen for 240 sec, and a curve is automatically plotted on the recorder following the blank run.
  - Sample run
  - Pipette 50 mL of sample into the sample cup by means of the microliter pipette.
  - Press the "Purge Time" key and enter a value of 420 with the numerical keys.
  - Press the "Sample" and "Run" keys.
  - The sample is automatically purged for 420 sec. Upon completion of the sample run, a sample curve is automatically plotted with the blank being subtracted. The peak potential and peak current values are also recorded.
  - Standard run.
  - Pipette 50 µL of $Na_2S_2O_3$ polarographic standard into the sample cup.
  - Press the "Purge Time" key and enter a value of 180 with the numerical keys.
  - Press the "Standard" and "Run" keys.

- The standard (including sample) run is initiated following a purge of 180 sec. Upon completion of the run, the curve is automatically played back with a listing of the peak potential and peak current values.
- Press the "Peak Potential" key and enter the peak potential listed on the standard playback.
- Press the "Peak Concentration" key and enter the known concentration of the standard (before dilution) in either PPB or PPM. (Conversion to actual PPB or PPM is not necessary. This enables the PPB or PPM result concentration of the sample to be read directly as g/L.)
- Press the "Standard" and "Playback" keys. The standard curve is played a second time, including a listing of the peak potential, peak current, and peak concentration. The second playback of the standard allows the standard concentration to be set up in the standard data files of the instrument.

• Sample playback

- Press the "Sample" and "Playback" keys. The sample curve is played back a second time, with a listing of the sample peak potential, peak current, and peak concentrations. The peak concentration (in PPB or PPM) can be read directly as g/L $Na_2S_2O_3$.

• Sample analysis (Sulfite treated)

- Pipette 10 mL of 0.5M acetate buffer into a clean sample cup and mount it onto the Model 303 SMDE.
- Run a "Blank" on the 0.5M acetate buffer polarographic medium.
- Press the "Purge Time" key and enter a value of 240 with the numerical keys.
- Press the "Clear Standard Data" and "Yes" keys.
- Press the "Blank" and "Run" keys.

- The polarographic medium is automatically purged with oxygen-free nitrogen for 240 sec, and a curve is automatically plotted on the recorder following the blank run.
- Sample run.
- Pipette 50 µL of "sulfite treated" sample into the sample cup with the microliter pipette.
- Press the "Purge Time" key and enter a value of 420 with the numerical keys.
- Press the "Sample" and "Run" keys.
- The sample is automatically purged for 420 sec. Upon completion of the sample run, a sample curve is automatically plotted, with the blank being subtracted. The peak potential and peak current values are also recorded.
- Standard run.
- Pipette 50 µL of $Na_2S_2O_3$ polarographic standard into the sample cup.
- Press the "Purge Time" key and enter a value of 180 with the numerical keys.
- Press the "Standard" and "Run" keys.
- The Standard (including sample) Run is initiated following a purge of 180 sec. Upon completion of the run, the curve is automatically played back with a listing of the peak potential and peak current values.
- Press the "Peak Potential" key and enter the peak potential listed on the standard playback.
- Press the "Peak Concentration" key and enter the known concentration of the standard (before dilution) in either PPB or PPM. (Conversion to actual PPB or PPM is not necessary. This enables the PPB or PPM result concentration of the sample to be read directly as g/L.)

- Press the "Standard" and "Playback" keys. The standard curve is played back a second time, including a listing of the peak potential, peak current, and peak concentration. The second playback of the standard allows the standard concentration to be set up in the standard data files of the instruments.

• Sample playback

- Press the "Sample" and "Playback" keys. The sample curve is played back a second time, with a listing of the sample peak potential, peak current, and peak concentration. The peak concentration (in PPB or PPM) can be read directly as g/L $Na_2S_2O_3$.

Calculation

• Polysulfide sulfur, as sulfur g/L = (g/L $Na_2S_2O_3$ after treatment - g/L $Na_2S_2O_3$ before treatment) x $(\frac{32.1}{158.1})$

MEAD AMALGAM METHOD

Introduction and Principles

The amalgam method is used by Central Research Development of The Mead Corporation for the analysis of Na_2S and elemental sulfur in polysulfide (PS) pulping liquors. The method was "originally proposed in Germany (55) and further developed by The Mead Corporation." The development of the method is described in Mead Chemical Systems Technical Bulletins numbers G-002A (April, 1975; revised Sept., 1975) and G-005 (Aug., 1977).

The Mead Amalgam Method is based upon the determination of sodium sulfide before and after the reduction of the polysulfide in the sodium amalgam. The determination of sodium sulfide requires the addition of Na_2SO_3 to the liquor/sample. The

Na_2SO_3 added reacts with the sodium polysulfide (Na_2S_x) to release the "bound" Na_2S as shown below.

$$Na_2S_x + (x-1)\ Na_2SO_3 \rightarrow (x-1)\ Na_2S_2O_3 + Na_2S$$

The total sodium sulfide is then determined by potentiometric titration using either $AgNO_3$ (Technical Bulletin G-002A) or $HgCl_2$ (Technical Bulletin G-005) as the titrant.

For the determination of polysulfide sulfur, a second liquor sample is treated with sodium amalgam to reduce polysulfide to sulfide as shown by the following equation:

$$Na_2S_x + (2x-2)\ NaHg_n \rightarrow x\ Na_2S + (2x-2)\ Hg_n$$

The sodium sulfide present (before and after reduction) is then potentiometrically titrated by $AgNO_3$ or $HgCl_2$. The difference in equivalent volumes between the two titrations is used to calculate the polysulfide sulfur content of the liquor.

In the following procedure, $AgNO_3$ was used as the titrant for the normal potentiometric titration of sodium sulfide.

Scope, Apparatus, Reagents, and Procedures

Scope

- This procedure describes a method which was further developed by Mead Chemical Systems for determining polysulfide content of various liquors (54).
- A manual potentiometric titration using 0.1N $AgNO_3$ titrant is conducted first for the determination of the sodium sulfide content of a liquor. Polysulfide in a second sample is then reduced with sodium amalgam to create additional sodium sulfide, followed by a second potentiometric

titration. The difference in equivalent volumes between the two titrations is used to calculate the polysulfide content of the liquor.

Apparatus

- pH meter with a millivolt scale
- Orion 94-16A sulfide-ion selective electrode or equivalent
- Orion 90-02 double junction reference electrode.
- 150-mL and 400-mL beakers
- 100-mL volumetric flask
- 10-mL and 20-mL transfer pipettes
- Disposable pipettes for decanting the sample from the amalgam
- 50-mL burette and burette stand
- Magnetic stirrer

Reagents

- 0.1N $AgNO_3$
- Concentrated ammonium hydroxide
- Na_2SO_3 crystals
- Sodium amalgam

Procedure

- Preparation of Sample
- Add about 50 mL of oxygen-free distilled water to a 100-mL volumetric flask.
- Pipette 20 mL of liquor sample into flask.
- Dilute to mark with oxygen-free distilled water.
- Flush the top of the flask with O_2-free nitrogen for about two minutes. Quickly stopper and mix well.

- Reduction of Polysulfide Sulfur to Sodium Sulfide
- To a 400-mL beaker, add 10 mL of distilled water, 10 mL of conc. NH_4OH, and 2 g Na_2SO_3. Place on magnetic stirrer to dissolve some of the crystals.
- To a clean, dry 150-mL beaker, add approximately 10 mL of previously unused sodium amalgam.
- Pipette 10 mL of diluted sample into the 150-mL beaker containing the amalgam. Gently swirl the beaker until the color becomes clear. Swirl for 1 minute more. Transfer quantitatively to the 400-mL beaker. Rinse the beaker 5 times with 30-50 mL of distilled water, transferring each rinse to the 400-mL beaker.
- Place the 400-mL beaker on a magnetic stirrer and adjust the rate of stirring just short of creating a vortex in the solution.
- Titrate potentiometrically using 0.1000M $AgNO_3$ and Orion 94-16A & 90-02 electrodes. Record mL equivalent volume 0.1000M $HgNO_3$ as volume B.
- Determination of Sodium Sulfide
- To a 400-mL beaker, add 10 mL concentrated NH_4OH, 2 g Na_2SO_3, and dilute to 150 mL with distilled water. Place the beaker on a magnetic stirrer and stir to dissolve the crystals. When the Na_2SO_3 crystals have dissolved, adjust the rate of stirring just short of creating a vortex in the solution.
- Pipette 10 mL of sample into the beaker.
- Titrate potentiometrically using 0.1000N $AgNO_3$ and Orion 94-16A & 90-02 electrodes.
- Record mL equivalent volume 0.1000N $AgNO_3$ as volume A.

Calculations

- A x 1.55 = g/L Na_2S, as Na_2O
- (B - A) x 0.8 = g/L polysulfide sulfur, as sulfur

Modifications

- This procedure contains several slight modifications of the Mead Amalgam Method.
- Modifications.
- Oxygen-free distilled water was used for dilution instead of distilled water. Oxygen-free nitrogen is passed through distilled water for 1 hr and then the container is stoppered tightly.
- Titration of the reduced sample is done before the titration of the unreduced sample.
- For each polysulfide reduction, fresh, previously unused amalgam in a clean, dry beaker is used.
- For the unreduced sample, the sample medium is added to the 400-mL beaker before the sample is added. The sample medium is prepared in the following order:
    1. Add 150 mL distilled water to the 400-mL beaker.
    2. Pipette 10 mL of concentrated NH_4OH into the beaker.
    3. Add 2 grams Na_2SO_3 crystals, then dissolve using magnetic stirring.
    4. Pipette 10 mL of liquor sample into the beaker.
- For the reduced sample, the sample medium is also added to the 400-mL beaker before the sample is added. To the 400-mL beaker, add about 10-20 mL distilled water. Pipette in 10 mL of NH_4OH. Add 2 grams Na_2SO_3 crystals and stir while the sample is being reduced. The reduced sample is then added.
- An Orion 90-02 double junction reference electrode is used instead of a saturated calomel electrode. Care is taken to prevent the electrode from touching or nearly touching the side of the beaker. The bottom of the electrode surface is rinsed thoroughly between titrations to remove any adherence of silver sulfide to the crevice located on the circumference of the bottom surface of the electrode.

TAPPI STANDARD 624 os-68

Scope

- This procedure describes polysulfide sulfur analysis of kraft white liquor using TAPPI STANDARD T 624 os-68.
- If the sample has been previously analyzed for sulfide, thiosulfate, and sulfite using T 624 os-68, the "S.F.R.C.$_b$" and "S.F.R.C.$_c$" determinations of the unreduced sample can be used for the polysulfide analysis. The preliminary testing for complete sulfide removal with $ZnCO_3$ may also be eliminated.
- Slight modifications of the TAPPI procedure have been made and are outlined later in this section.

Apparatus

- pH meter equipped with a millivolt scale
- Platinum and saturated calomel electrodes
- 250-mL volumetric flasks
- Büchner funnel and suction flask, each 500 mL
- Wattman No. 40 ashless filter paper
- 50-mL burette and burette stand
- Magnetic stirrer/hot plate and a Teflon-covered magnetic stirring bar
- 5, 10, 15, and 25-mL pipettes
- 250-mL Erlenmeyer flasks

Reagents/Indicators

- 0.2N and 0.15N standard iodine solutions
- 0.1N standard $Na_2S_2O_3$
- 20% H_2SO_4
- Thyodene as a starch indicator
- 1M $ZnSO_4$
- 1M Na_2CO_3

- Freshly prepared ammoniacal silver nitrate
- 12M NaOH

Procedure

- SULFIDE-FREE REDUCING COMPOUNDS, "S.F.R.C." (unreduced sample)
- Removal of Sulfide
- Make a preliminary test on an aliquot of the liquor to determine the amount of zinc carbonate required for complete sulfide removal as follows: Pipette 25 mL of liquor into a 250-mL volumetric flask. Add a freshly prepared suspension of $ZnCO_3$ made by mixing 40 mL each of 1M $ZnSO_4$ and 1M Na_2CO_3 to the volumetric flask. Mix the contents well by swirling the flask. Dilute to mark with distilled water while gently swirling the contents of the flask. Filter using a Büchner funnel, suction flask, and Wattman No. 40 ashless filter paper. Add a drop of freshly prepared ammoniacal silver nitrate to the clear filtrate. If a brown or heavy cloud forms in the filtrate, precipitation is incomplete. Repeat the procedure using $\pm$ 5 mL of the original volumes of 1M $ZnSO_4$ and 1M Na_2CO_3 until the amount of $ZnCO_3$ suspension required to completely remove sulfide has been determined.
- Pipette 25 mL of liquor into a 250-mL volumetric flask and add the entire amount of $ZnCO_3$ suspension necessary to completely remove sulfide as determined above. Dilute to mark with distilled water while gently swirling the contents of the flask.
- Filter using a Büchner funnel, suction flask, and Wattman No. 40 ashless filter paper.
- Oxidation with Iodine ("S.F.R.C.$_b$")
- Pipette 15 mL of standardized 0.2N iodine solution into a 250-mL Erlenmeyer flask.

- Pipette 5 mL of 20% H_2SO_4 into the flask.
- Pipette 25 mL of the clear filtrate into the acidified iodine while vigorously swirling the contents of the flask.
- Titrate the excess iodine with 0.1N $Na_2S_2O_3$, adding 1 or 2 microspatulas of thyodene near the end point (faint yellow color).
- Oxidation with Hypoiodite ("S.F.R.C.$_c$")
- Add 50 mL of 12M NaOH to a 150-mL beaker containing a Teflon-covered magnetic stirrer bar.
- Pipette 25 mL of clear filtrate into the beaker.
- Place the beaker on a magnetic stirrer and adjust the rate of stirring so as not to create a vortex or whip air into the solution.
- Titrate the sample potentiometrically using 0.15N iodine titrant, a pH meter, and platinum and saturated calomel electrodes. The initial millivolt reading should be between -100 and -300 mV. The solution is titrated until a zero or slight (+5) millivolt reading is obtained.
- SULFIDE-FREE REDUCING COMPOUNDS, "S.F.R.C." (reduced sample)
- Reduction of polysulfide sulfur
- Pipette 25 mL of liquor into a 150-mL beaker.
- Add 0.5 g Na_2SO_3. Warm to about 50°C until the yellow color disappears. Cool to room temperature. Transfer quantitatively to a 250-mL volumetric flask.
- Add the entire amount of $ZnCO_3$ necessary for complete sulfide removal (determined previously).
- Dilute to mark and mix well.
- Filter using a Büchner funnel, suction flask, and Wattman No. 40 ashless filter paper.
- Determine "S.F.R.C.$_b$" of the reduced sample.
- Determine "S.F.R.C.$_b$" of the reduced sample.

Data/Calculation

- Record all data as needed.
- Calculations.
- Sulfide-free reducing compounds (unreduced and reduced samples)

$$\text{"S.F.R.C.}_b\text{" eq/liter} = \frac{(\text{mL } I_2 \times N I_2) - (\text{mL } Na_2S_2O_3 \times \text{N } Na_2S_2O_3)}{2.5}$$

$$\text{"S.F.R.C.}_b\text{" eq/liter} = \frac{\text{mL } I_2 \times N I_2}{2.5}$$

- Sodium thiosulfate (reduced and unreduced samples)

$$Na_2S_2O_3 \text{ g/L} = \frac{(\text{"S.F.R.C.}_c\text{"} - \text{"S.F.R.C.}_b\text{"}) \times 158.1}{7}$$

- Sodium thiosulfate (reduced and unreduced samples)

$$Na_2S_2O_3 \text{ g/L} = \frac{(\text{"S.F.R.C.}_c\text{"} - \text{"S.F.R.C.}_b\text{"}) \times 158.1}{7}$$

- Polysulfide sulfur

$$\text{g/L polysulfide sulfur} = [(Na_2S_2O_3 \text{ g/L of reduced sample} - Na_2S_2O_3 \text{ g/L of unreduced sample})] \times \left(\frac{32.1}{158.1}\right)$$

Modifications of T 624 os-68

- The volume of liquor used in determining sulfide-free reducing compounds was changed from 50 mL to 25 mL.
- As a result of this modification, the denominator in the calculation for both "S.F.R.C.$_b$" and "S.F.R.C.$_c$" was changed from 5 to 2.5.
  - The starting volumes of 1M $ZnSO_4$ and 1M Na_2CO_3 were changed from 15 mL to 40 mL.
  - For making the preliminary test for complete removal of sulfide, the filtration step was added to decrease the time needed to make the determination